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HYGROSCOPIC EQUILIBRIA FOR HULLS AND KERNELS OF SUNFLOWERSEED AND OATS[1]

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Abstract

An apparatus for adjusting a stream of air to definite relative humidities using saturated salt solutions and the application of this equipment to the determination of hygroscopic moisture in grains is described. Data are presented to show that under equilibrium conditions sunflower hulls have a higher moisture content than meats. For oats this condition is reversed. In the lower humidity ranges sunflower and oat hulls show similar moisture contents, which fall about 2% below the values for wheat, oat groats, flax, and sunflower meats computed to an oil-free basis. It is concluded that hygroscopic equilibria in grains are governed more by the structure of the grain and physical absorption phenomena than by the chemical components.

In previous studies on sunflowerseed and oats (4, 7) differences in moisture level between hulls and meats were observed. This is not surprising, since a marked difference exists in the composition of these two parts of the seed. The hulls of both sunflowerseed and oats are composed mainly of cellulose, hemicelluloses, and lignin and should behave similarly, but the meats differ markedly from the hulls in their components and should show a difference in moisture absorption. Furthermore, since sunflower meats and oat groats differ greatly in composition, it would be expected that this difference would be reflected in their moisture holding capacity.

Since the moisture distribution between meats and hulls is related to the problem of dehulling (4), it appeared of practical interest to investigate this relation.

Methods and Materials

In a previous study (4) samples were exposed to constant relative humidities by supporting them over saturated salt solutions at a controlled temperature of 25° C. At high humidities it required two to three weeks for diffusion processes to establish equilibrium between the seed and the surrounding air. Under these conditions, difficulties were encountered due to mould growth on the samples (5).

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To hasten the establishment of equilibrium conditions the apparatus shown in Fig. 1 was devised. This consists of a prehumidifier, *A*, constructed from a milk bottle with a sintered glass disk in the inlet tube; a humidification tower, *B*; a spray trap, *C*; a sample tube, *D*; and a vacuum ballast fitted with a vacuum regulator. Final adjustment of humidity is accomplished in tower *B* by means of saturated salt solutions.

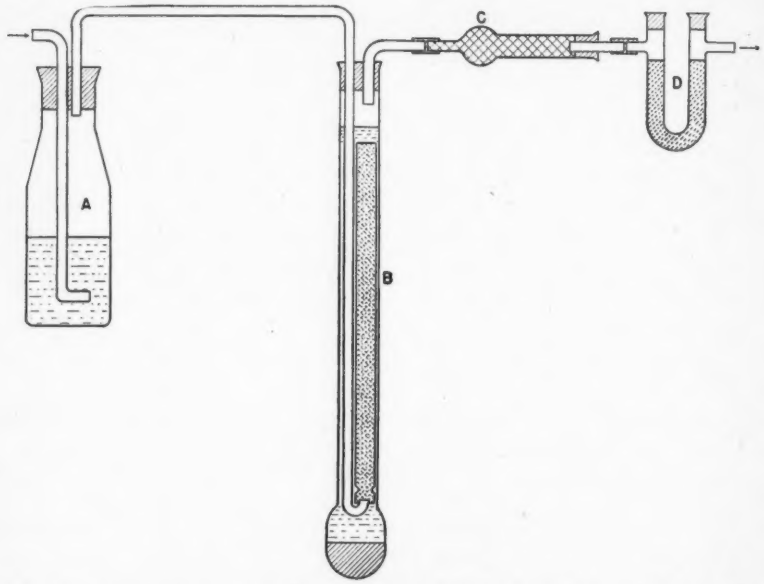

FIG. 1. *Apparatus for obtaining constant humidity in establishing hygroscopic equilibria.*

An inner tube filled with glass beads is supported in tower *B* by means of the air inlet tube. Some solid salt is placed in the bottom of *B*, which is then filled to the top of the inner tube with a saturated solution of the required salt. In operation, air aspirated through the bead column induces a circulation of the solution, which passes up through the bead column and down the outer jacket where it comes in contact with solid salt at the bottom of tower *B*. This action insures that the solution will always be saturated and that no supersaturation will occur owing to quiescent evaporation that might occur in a static system.

When air is fed directly to the humidifying tower, evaporation from the solution causes crystallization to occur in the inlet tubes with plugging of the system. To overcome this difficulty a prehumidifier was introduced and charged with a solution not quite saturated with respect to the salt being used in the tower. To obtain the higher humidities, 81% and 93%, pure water was used in the prehumidifiers since the normal room humidity was in the order of 30 to 40%.

A battery of five units was set up in a room thermostatically controlled at 25° ± 2° C. The units were all connected to a common vacuum ballast and air flow through each unit adjusted to 500 ml. per hr. by means of capillaries in the lines.

As a check on the effectiveness of humidity control, a volumetric hygrometer (1) was constructed and measurements were made of actual humidities obtained. The salts used, together with humidities as given in the International Critical Tables and experimentally determined values, are shown in Table I. The theoretical values and those actually produced by the equipment agree within the experimental error of the volumetric hygrometer.

TABLE I

RELATIVE HUMIDITIES OF SATURATED SALT SOLUTIONS AT 25° C.

Salt	Relative humidity, %	
	From Tables	Experimental
$CaCl_2 \cdot 6H_2O$	31.0	31.0
K_2CO_3	43.0	43.0
$Ca(NO_3)_2$	51.0	50.0
NH_4NO_3	62.0	60.5
$NH_4Cl + KNO_3$	71.2	71.0
$(NH_4)_2SO_4$	81.1	80.0
$NH_4H_2PO_4$	93.0	91.5

A sample of the material under study was placed in the U-tube, *D*, which was then connected in the aspiration system. At intervals the tube was removed, the arms closed, and the tube weighed. When constant weight was obtained, usually after five to six days, the sample was removed and moisture determined in a vacuum oven at 100° C. with a 16 hr. heating period.

It requires several days before mould growth begins at high moisture levels and only in a very few cases at the highest humidity levels was there any evidence of moulding.

The sunflower samples used were of the Mennonite variety from experimental plots at the University of Saskatchewan. The seed was harvested at high moisture content (25 to 30%) and air-dried in the laboratory to a level of 4.5 to 5.0%. At this value the hull composed 45 to 50% and the meats 50 to 55% of the kernel weight.

Victory oats grown at the University of Saskatchewan were used for the study. The sample had a bushel weight of 45 lb. and was composed of 26.3% hulls and 73.7% groats.

Since it is obviously impossible to dehull seed at high moisture levels without loss of moisture, hygroscopic equilibria were determined on whole seed and on meats and hulls after separation. The sunflower seed was carefully hulled by hand for initial studies, but subsequent work indicated that hulls separated

mechanically gave almost identical results if care was used to exclude all traces of meats. The oats were dehulled with a mechanical huller (7) and the final samples of groats and hulls were carefully hand-picked.

Results

Sunflowerseed

Three samples of sunflowerseed were studied and the mean equilibrium moisture values for whole seed, meats, and hulls are shown graphically in Fig. 2. The actual values together with differences between meats and hulls are given in Table II. If moisture contents of the hulls and meats are plotted against moisture content of the whole seed, two virtually straight lines are

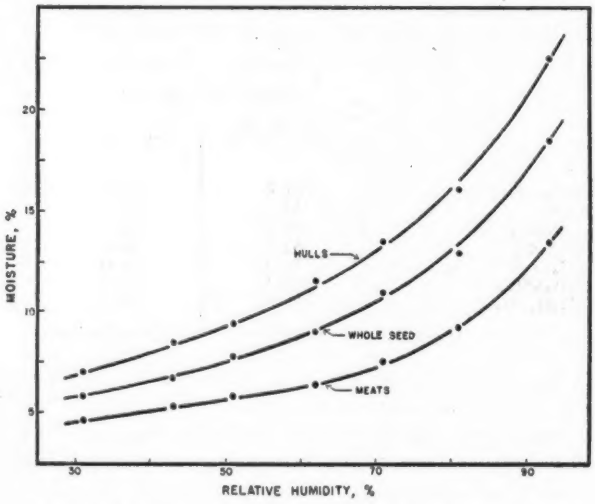

FIG. 2. *Relation of the hygroscopic moisture in whole sunflowerseed, meats, and hulls to various relative humidities at 25° C.*

TABLE II

RELATION OF EQUILIBRIUM MOISTURE CONTENT OF SUNFLOWERSEED, SUNFLOWER HULLS, AND SUNFLOWER MEATS TO RELATIVE HUMIDITY AT 25°C.

Relative humidity, %	Moisture content, %			
	Whole seed	Hulls	Meats	Difference, hulls minus meats
31.0	5.8	7.0	4.7	2.3
43.0	6.7	8.4	5.3	3.1
51.0	7.8	9.3	5.8	3.5
62.0	9.0	11.6	6.4	5.2
71.2	11.0	13.6	7.6	6.0
81.1	12.9	16.2	9.2	7.0
93.0	18.5	22.6	13.5	8.1

obtained that diverge by the amount shown in the last column of Table II. This indicates that the distribution of moisture between meats and hulls is directly proportional to the total moisture of the seed.

A comparison of the curve for whole sunflowerseed with that obtained by Larmour, Sallans, and Craig (4) shows that the moisture values obtained in the present study are higher, especially at higher humidities. This may be due in part to the use of an aspiration instead of a static system for production of controlled humidities. However, it seems more probable that the main difference is caused by differences in the samples of seed used. For example, in the present study values of 5.4, 5.7, and 6.3% moisture were obtained at a relative humidity of 31%. Similar differences were observed at all the other humidity levels.

It appears that differences in kernel content of the seed and oil content of the meats must have an effect on the equilibrium moisture values. The data on hulls for the three samples showed much closer agreement than similar values for whole seed and meats, although one sample was consistently slightly higher than the other two. Since the hulls are composed mainly of cellulose and lignin and both of these materials appear to have similar moisture holding capacities, little variation in the equilibrium moisture values would be expected. For whole seed the oil content is approximately 25% and for meats, 50%. Since the oil has little, if any, tendency to absorb moisture, variations in the quantity present would alter the proportion of hygroscopic material with a resultant shift in equilibrium moisture values for whole seed and meats.

Oats

The data obtained for oats using a single sample are presented graphically in Fig. 3 and the differences between hulls and groats are shown in Table III. As with sunflowerseed a plot of hull and groat moistures against moisture content of the whole seed gives two straight lines. However, in this case the lines are virtually parallel as indicated by the constant difference between groats and hulls shown in the last column of Table III.

TABLE III

RELATION OF EQUILIBRIUM MOISTURE CONTENT OF OATS, OAT HULLS, AND OAT GROATS TO RELATIVE HUMIDITY AT 25° C.

Relative humidity, %	Moisture content, %			
	Whole seed	Groats	Hulls	Difference, groats minus hulls
31.0	8.1	8.6	7.3	1.3
43.0	9.2	9.7	8.4	1.3
51.0	10.0	10.6	9.1	1.5
62.0	11.2	11.9	10.5	1.4
71.2	12.6	13.2	11.8	1.4
81.1	14.7	15.4	14.0	1.4
93.0	20.2	20.8	19.4	1.4

The other striking difference between oats and sunflowerseed is that with oats the meats have a higher moisture holding capacity at equilibrium than the hulls. This is just the reverse of the results obtained with sunflowerseed. Apparently these differences in behaviour are due mainly to differences in oil content of the various materials.

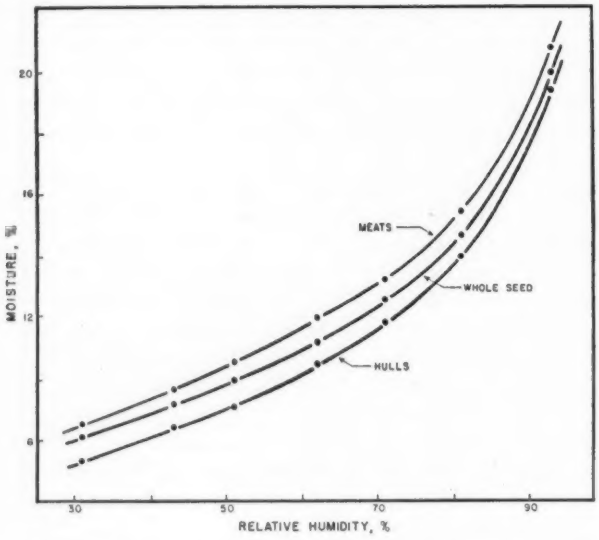

FIG. 3. *Relation of the hygroscopic moisture in oats, oat hulls, and oat groats to various relative humidities at 25° C.*

Relation of Hygroscopicity to Grain Constituents

In their studies on cereal grains Coleman and Fellows (2) were unable to relate differences in hygroscopic equilibria of grains to protein content. Subsequently Ramstad and Geddes (6) postulated differences in ash content as a possible cause of these differences. In their study Larmour, Sallans, and Craig (4) found that differences in ash content would not explain the differences in hygroscopicity of oil seeds when calculated to an oil-free basis and suggested that, "any adequate explanation of these differences will likely have to be found in the nature of the components of these seeds rather than in the actual amounts of the various components present".

In Table IV are collected data on sunflower hulls, oat hulls, wheat, oat groats, flax, and sunflower meats. Since oil does not absorb moisture, the values for oat groats, flax, and sunflower meats are expressed on an oil-free basis to facilitate comparison. Moisture values for wheat were estimated from the data of Coleman and Fellows (2), and values for flax were taken from the work of Larmour, Sallans, and Craig (4). The last two lines in the

TABLE IV

COMPARISON, ON AN OIL-FREE BASIS, OF THE HYGROSCOPICITY OF WHEAT, OAT GROATS, FLAX, SUNFLOWER MEATS, SUNFLOWER HULLS, AND OAT HULLS

Relative humidity, %	Moisture content, oil-free basis					
	Wheat	Oat groats	Flax	Sunflower meats	Sunflower hulls	Oat hulls
31.0	9.4	9.2	8.9	9.0	7.0	7.3
43.0	10.8	10.4	10.6	10.1	8.4	8.4
51.0	11.9	11.4	11.4	11.0	9.3	9.1
62.0	14.0	12.7	13.3	12.0	11.6	10.5
71.2	16.3	14.1	15.2	14.1	13.6	11.8
81.1	20.0	16.4	18.6	16.8	16.2	14.0
93.0	27.1	22.1	26.3	24.0	22.6	19.4
Protein, % (oil and moisture-free)	14.1	18.9	45.0	52.4	3.8	4.1
Ash, % (oil and moisture-free)	1.93	2.06	6.89	8.47	2.68	6.23

table show protein and ash content calculated to an oil- and moisture-free basis from average values for these materials (8).

The striking feature of the data is the close agreement in hygroscopic equilibria at low moisture values for all these materials, which differ so widely in composition. At humidities of 31.0, 43.0, and 51.0% the values for wheat, oat groats, flax, and sunflower meats are virtually the same even though the protein content differs by as much as 38%. Such variations as do occur bear no relation to total protein. A similar situation exists with respect to ash content. The only evidence that chemical composition may affect hygroscopicity is found in the case of oat and sunflower hulls. These materials show equivalent moisture holding capacities up to a relative humidity of 51%. However, their moisture values are approximately 2% lower than those for the other materials shown in Table IV. It would appear that radical changes in chemical composition, such as substitution of 50% protein for 50% cellulose, would be required to alter the hygroscopic moisture equilibrium at low relative humidities. Only the widest extremes in chemical composition of the material affect the moisture holding capacity.

This behaviour suggests that the water holding capacity is due to physical rather than chemical forces and that any adequate explanation for hygroscopic equilibria must consider grains as colloidal or gel systems. The observation that materials differing as widely in composition as wheat and sunflower kernels show similar hygroscopic equilibria up to a relative humidity of 51% or a moisture level of about 11.5% suggests that in this region the moisture may correspond to 'bound water'. Above this level the rate of moisture absorption with increasing humidity appears to be characteristic of the particular material under study. If it is assumed that 'capillary water' or 'water of imbibition' is present in this range, 'solvation' would occur and

differences in the amounts of soluble electrolytes and organic constituents would begin to affect the water absorbing characteristics of the gel structure.

It is obvious that the hygroscopic behaviour of grains is a complicated phenomenon and no simple interpretation based on a single factor will provide an adequate explanation. However, it is interesting to note that Fairbrother (3) reports a linear relation between moisture content of wheat flour and relative humidities between 15 and 90%. Above 90% relative humidity a sharp rise in moisture uptake with increasing humidity was observed. In view of the results reported above it is difficult to conceive that this marked difference between the behaviour of wheat and flour can be explained on the basis of chemical constitution. However, since the cellular structure of wheat is destroyed in the milling process, it appears quite logical to attribute the difference in hygroscopic behaviour to changes in the physical state of the material. This may be taken as further evidence that the main factors influencing hygroscopicity of grains are colloidal and are related to the physical structure of the grain.

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FLASH DRYING IN RELATION TO HULLING OF SUNFLOWERSEED AND OATS[1]

By G. D. Sinclair[2] and H. R. Sallans[3]

Abstract

A laboratory flash drying unit with continuous feed is described. In tests on sunflowerseed and oats it was possible to lower the moisture content of the hulls several units per cent without appreciably changing the moisture content of the meats. The effect of this change in the moisture distribution between meats and hulls on hulling efficiencies was studied. It was found that flash drying gave a slightly lower percentage of seed hulled with a definite decrease in the percentage of meats broken. Furthermore, the damaged meats were not broken into as small pieces and hence separation of meats and hulls was facilitated.

Results of hygroscopic moisture studies on sunflowerseed and oats (1) have shown that a definite difference in moisture content exists between the kernels and the hulls. With sunflowerseed the moisture level in the hulls is higher than that in the meats, while with oats this distribution is reversed. It was suggested (3) that the ideal way to secure a high percentage of hulling with minimum breakage of meats was to have the hull dry and brittle with the meats moist and tough.

Preliminary experiments on drying small samples of sunflowerseed in an air oven with forced circulation showed that the normal moisture distribution between meats and hulls could be changed by short periods of drying at moderate temperatures. It was possible under favourable conditions to reduce the moisture content of hulls several per cent without changing the meat moisture appreciably. In view of these findings, it was decided to construct a small unit to study the effects of flash drying in relation to hulling. Since oats are often pan dried before hulling and the normal moisture distribution is the opposite to that in sunflowerseed, it appeared that data on oats would be of value in assessing the utility of flash drying.

To produce the maximum drying of the hull with a minimum change in the moisture content of the meats, it is necessary to subject the seed to a short, sharp heating period and to dehull it promptly before moisture diffuses from the kernel back into the hull. In preliminary trials the seed was dropped directly from the heating unit into the huller. This was unsatisfactory as the hulls seemed to sweat on cooling slowly. A greater moisture differential between meats and hulls was obtained by cooling the seed in a blast of air immediately after heating.

The design of the unit and data on changes in moisture distribution and hulling efficiencies are presented in the following sections of this paper.

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Equipment

A section drawing of the flash drying unit is shown in Fig. 1. A three bladed 6 in. centrifugal fan, *F*, is connected to a duct containing two flues. The upper one opens into the drying chamber, *B*, and is heated by four 660-w. cone type heaters while the lower one opens into cooling chamber *C*. A feed hopper, *A*, is mounted above drying chamber *B* and a release roll is mounted below cooling section *C*.

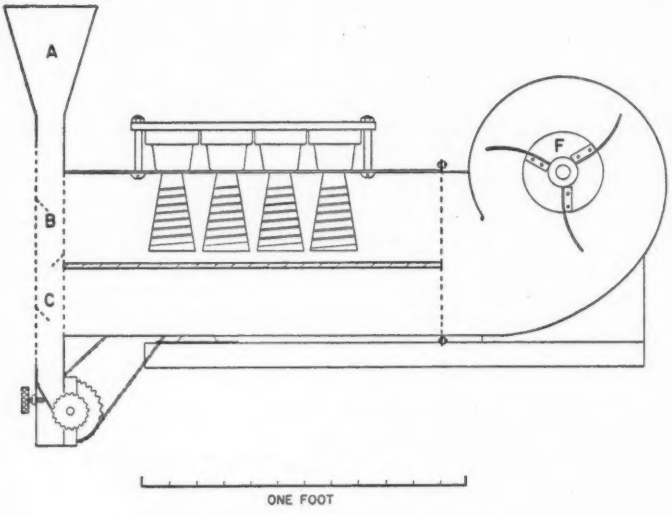

FIG. 1. *Section drawing of flash drying unit.*

The blades of fan *F*, made of 16-gauge sheet metal, are mounted on a steel flange carried on the shaft of a $\frac{1}{4}$ h.p., d-c. motor. Regulation of air flow is obtained by adjustable slides on the air inlet to the fan housing. This housing, having an air outlet 3 in. by 6 in., is fabricated from 20-gauge sheet metal and is bolted to the heating and cooling ducts. A sheet of galvanized screen with 1/16 in. perforations is inserted between the fan and air ducts to provide a back pressure and thus give a uniform distribution of air. The heating and cooling ducts, made of 20-gauge galvanized iron, are separated by a 3/16 in. transite board and the whole unit is covered with 10 layers of heavy asbestos paper. The drying and cooling unit is faced with galvanized screen having 1/16 in. openings and carries three horizontal fins to mix the seed as it passes through the dryer. The inner screen area, 3 in. $\times$ 6 in., is smaller than the outer area, 3 in. $\times$ 8 in., to provide a pressure drop across the unit. This facilitates a uniform rate of feed and prevents clogging. A grooved wooden release roll is chain driven from a 1/30 h.p. variable speed motor that can be reduced to 30 r.p.m. Feed rate is controlled by adjusting the clearance between the roll and a hinged metal flap by means of a thumbscrew.

After a few preliminary trials the equipment was adjusted to give an air temperature of 190° to 195° C. when no seed was passing through chamber *B*. Air velocity under these conditions was 400 to 410 linear feet per minute in both the heating and cooling sections. When the unit was filled with sunflowerseed the air velocity was 250 ft./min. and with oats 240 ft./min. as measured with an anemometer. Actual operating temperatures recorded by a thermometer inserted in the centre of heating section *B* varied from 121° C. to 175° C. depending on the moisture content of the seed and the rate of feed.

Materials and Methods

Sunflowerseed

A two bushel lot of No. 1 C.W. Mennonite sunflowerseed, 52.5% meats (dry basis), was obtained from a local processing firm. After careful cleaning to remove trash, the sample had a bushel weight of 26.4 lb. and was of fairly uniform seed size. The bulk sample was thoroughly blended in a rotary mixer and quartered. The main samples were tempered to moisture levels of 8.0, 9.4, 10.6, and 12.2%. After tempering, each of these samples was divided into four equal parts to provide material for four drying rates.

Oats

Two bushels of commercial Banner oats of seed grade, 68.8% groats (dry basis), was obtained from the Field Husbandry Department at the University of Saskatchewan. The sample as received was cleaned to seed specifications and had a bushel weight of 41.9 lb. After thorough mixing it was subdivided as for sunflowerseed, but the moisture levels selected were 9.8, 12.0, 14.1, and 16.3% since oats normally have a higher percentage of moisture than sunflowerseed (1).

Drying

The drying portion of the unit, consisting of both the heating and cooling sections, was found to hold 175 gm. of sunflowerseed or 278 gm. of oats. The release was set so that these quantities of material passed through the drying unit in 0.5, 1.0, 1.5, and 2.0 min., respectively, for the tests on both sunflowerseed and oats at each moisture level. It follows that the drying times recorded represent the time for the seed to pass through both heating and cooling sections of the dryer. Furthermore, the actual exposure of the seed to air at 190° to 195° C. is just a little greater than half the total drying time. For example, a drying time recorded as 0.5 min. represents 17 to 18 sec. heating followed by 12 to 13 sec. cooling. Under these conditions it was observed that the meats were only slightly warmed. On exposure for 70 sec. in the longest drying time of 2.0 min. there was no indication of damage to the meats in either sunflowerseed or oats even at the lowest moisture level of the feed.

Before starting a test the dryer was allowed to run till it was thoroughly heated, and seed was then fed continuously until a thermometer inserted in chamber *B* showed a constant reading. At this point samples were taken

for determinations of moisture content and hulling efficiency. Samples were hulled immediately after drying, only sufficient time being taken to weigh a 100 gm. aliquot.

Hulling

Tests on hulling efficiency were made with a laboratory huller and the methods of estimating percentage of seed hulled and meats broken have been described (3). A huller speed of 3000 r.p.m. was used for sunflowerseed and 3400 r.p.m. for oats.

Determination of Moisture

Determination of moisture content on the whole seed presented no difficulty. In the hulling and fanning operations, however, it is obvious that, if the relative humidity of the laboratory air differs markedly from that in equilibrium with the moisture content of the seed (1, 2), the values obtained for meats and hulls will not represent the moisture distribution in the seed at the time of impact in the huller. Moisture content of the hulls was found to change markedly on fanning, but tests on sunflower meats indicated that fanning produced only small changes, 0.2 to 0.3%, in moisture level. Hence, values for moisture content in the hulls were computed from data on meat moisture, whole seed moisture, and kernel percentage of the seed.

Results

Drying

Data on sunflowerseed at four moisture levels and four drying treatments are shown in Table I. If the moisture contents of the tempered undried sunflower samples are compared with equilibrium moistures from hygroscopic studies (1) it is found that 8.0, 9.4, 10.6, and 12.2% moisture in the whole seed correspond with relative humidities of 53, 64, 71, and 78%. It will also be noted that the moisture values for meats are consistently lower than those given in the previous data, while the hulls are consistently higher. This would be expected since the sample used in the present investigation had a higher percentage of kernels than the samples previously used, 52.5% as compared with about 47%.

Since little, if any, loss in moisture content of the sunflower meats occurred during hulling and fanning, it is apparent that the moisture distribution between meats and hulls of the tempered samples corresponded to equilibrium conditions.

Results for oats appear in Table II. From comparison with hygroscopic data (1) it appears that normal oat moistures of 9.8, 12.0, 14.1, and 16.3% should be in equilibrium with relative humidities of 48, 67, 78, and 86%. An examination of the data for hulls and groats shows that at a moisture level of 9.8% the values agree with those expected from previous work. However, as the moisture content is increased, there is an apparent reversal in moisture distribution, i.e., at 14.1% and 16.3% the hulls are higher in moisture than the groats. This is due to relatively rapid drying of the oat groats in hulling

TABLE I

THE EFFECT OF FLASH DRYING ON THE MOISTURE DISTRIBUTION BETWEEN SUNFLOWER MEATS AND HULLS AND ON HULLING EFFICIENCIES

Moisture in original seed, %	Drying time, min.	Moisture in dried seed, %			Hulling, %	Broken meats, %
		Whole seed	Meats	Hulls		
8.0	0.0	8.0	5.7	10.4	91.4	16.8
	0.5	7.1	5.6	8.6	91.8	17.2
	1.0	6.1	5.5	6.7	94.4	23.3
	1.5	5.0	5.1	5.0	94.4	25.5
	2.0	4.6	4.8	4.4	97.3	32.1
9.4	0.0	9.4	6.3	12.7	87.9	10.2
	0.5	8.1	6.4	9.9	86.8	12.0
	1.0	7.3	6.3	8.5	91.0	16.5
	1.5	6.1	6.0	6.3	94.4	22.2
	2.0	5.5	5.8	5.2	96.4	23.8
10.6	0.0	10.6	7.3	13.9	79.2	4.3
	0.5	9.7	7.3	12.2	83.7	6.8
	1.0	8.5	6.9	10.2	89.1	11.9
	1.5	7.4	6.8	8.1	89.5	13.3
	2.0	6.0	6.4	5.6	93.7	17.6
12.2	0.0	12.2	8.0	16.4	69.0	2.3
	0.5	10.6	8.0	13.2	68.2	3.9
	1.0	9.4	7.7	11.2	80.0	6.1
	1.5	7.8	7.4	8.3	86.8	9.4
	2.0	6.6	7.0	6.3	90.8	13.0

TABLE II

THE EFFECT OF FLASH DRYING ON THE MOISTURE DISTRIBUTION BETWEEN OAT GROATS AND HULLS AND ON HULLING EFFICIENCIES

Moisture in original seed, %	Drying time, min.	Moisture in dried seed, %			Hulling, %	Broken meats, %
		Whole oats	Groats	Oat hulls		
9.8	0.0	9.8	10.5	8.2	94.9	20.3
	0.5	9.3	10.4	6.6	93.6	12.6
	1.0	9.0	10.2	6.3	95.0	15.9
	1.5	7.8	9.5	4.0	96.2	22.0
	2.0	7.6	9.2	3.7	98.8	32.8
12.0	0.0	12.0	12.1	11.6	87.3	8.8
	0.5	11.3	12.1	9.3	86.4	6.8
	1.0	10.5	11.6	8.0	90.8	8.0
	1.5	9.4	11.0	5.7	94.6	15.8
	2.0	8.4	10.3	4.0	96.6	22.7
14.1	0.0	14.1	13.8	14.8	75.0	3.6
	0.5	13.4	13.7	12.8	77.4	4.1
	1.0	12.3	13.1	10.3	87.0	6.1
	1.5	11.4	12.4	9.3	92.2	12.0
	2.0	9.9	11.2	6.9	96.8	22.5
16.3	0.0	16.3	15.4	18.3	63.9	2.6
	0.5	15.2	15.2	15.2	71.0	1.9
	1.0	14.1	14.8	12.4	82.2	2.9
	1.5	12.3	13.7	9.0	92.6	8.9
	2.0	10.9	12.8	6.0	93.8	16.1

and fanning, which results from a higher surface to volume ratio and a lower oil content than is found in sunflower meats.

The data on moisture distribution in Tables I and II show clearly that it is possible by means of flash drying to reduce the moisture levels in both oats and sunflowerseed to a marked degree without appreciably affecting the moisture level in the meats. The degree of drying is obviously a function of the original moisture level in the seed and the drying time.

To facilitate comparison of the data on moisture distribution, mean values at each drying rate over all four initial moisture levels are shown graphically in Fig. 2 for both sunflowerseed and oats. The most striking and interesting feature is the close similarity in drying rate between sunflower and oat hulls. In both cases the initial moisture content of approximately 13.0% dropped rapidly in an almost linear relation with drying time. The curves for sunflower and oat hulls in Fig. 2 are almost parallel and in both cases the moisture drop was exactly 8.0%.

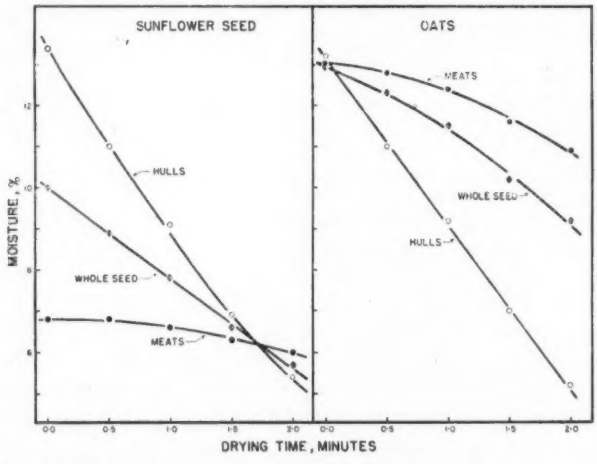

FIG. 2. *Distribution of moisture between hulls and meats of sunflowerseed and oats for various levels of flash drying.*

The moisture drop for oat groats is 2.1% while that for sunflower meats is only 0.8%. Since oat groats at 13% moisture are in equilibrium with a relative humidity of approximately 73% while for sunflower meats at 6.8% the corresponding value is 68%, the observed difference in drying rate cannot be due to differences in the moisture holding capacity of the two materials. It would seem that there is a greater transfer of moisture from the groats through oat hulls than from meats through sunflower hulls.

With sunflowerseed a drying time of two minutes produced a change in the differential moisture level between hulls and meats of + 6.4 to −0.6, or a total change of 7.0%; the corresponding value for oats was from −0.2 to −5.7, or a total of 5.5%.

Hulling

Data showing the percentage of seed hulled and meats broken at each drying level are shown in Table I for sunflowerseed and in Table II for oats. It will be noted that for sunflowerseed there is a consistent increase in the percentage of seeds hulled with increased drying time, but this is accompanied by an increase in the percentage of meats broken. With oats a similar trend is evident; however, at the lower moisture ranges, 9.8 and 12.0%, there appears to be a drop in broken meats for the shorter drying times.

To facilitate comparison of hulling efficiencies for flash-dried seed with those for seed having a normal moisture distribution, mean values over the four initial moisture ranges are plotted against percentage moisture in Fig. 3.

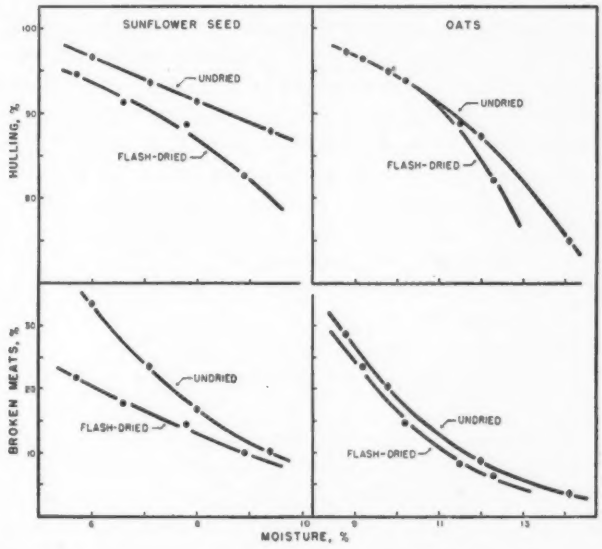

FIG. 3. *Relations of percentage seed hulled and meats broken to moisture content of normal and flash dried sunflowerseed and oats.*

The curve representing the percentage hulling for flash-dried seed falls below that for seed having normal moisture distribution. At 5.5% total moisture the flash-dried seed shows 2% less hulling while at 9.0% the difference is 10.0%. Data for percentage of broken meats in the lower figure show that at 5.5% moisture there is a reduction of 11% in breakage due to flash drying, but at 9.0% this difference falls to 2.0%. The same general trend is shown for the data on oats, but the differences between dried and undried samples are considerably smaller than those for sunflowerseed.

It should be noted that the broken meats from flash-dried samples were not broken into as small pieces as those from samples having a normal moisture distribution. Hence, in any recovery system involving fanning there would

be an appreciably greater recovery of oil-bearing material from flash-dried seed than the analytical figures quoted would indicate.

Discussion

It has been shown that the normal differential in moisture content between hulls and meats can be radically changed by means of flash drying. The primary objective of securing drier hulls with moister meats was attained. However, data on hulling efficiencies show that the expected result of higher percentage hulling at comparable moisture levels was not realized.

Normally in Mennonite sunflowerseed the meat is held firmly to the hull at one or more points of contact, while there is free space between the meat and hull over the remaining area. If there is free space under the point of impact in the huller, the hull crumples and cracks under the impact with little damage to the meat. When seed is flash dried, the hull tends to shrink with no compensating decrease in volume of the meat. Under these conditions the hull area not directly in contact with the meat is reduced and even though the hull is drier and more brittle the additional support furnished by the meat tends to resist the shattering effects of impact. In addition sunflower hulls have a light, spongy interior lining that is particularly susceptible to changes in moisture content. When seed is flash dried the atmosphere between the hull and meat becomes saturated with moisture at elevated temperatures. When it is cooled this moisture condenses in the spongy lining of the hull, which becomes tough. Even though the outer hull may become more brittle the shattering effect of impact is lessened by the tough inner lining with the result that the seed cracks but the hull is not completely freed from the meat.

In oats there is less free space between the meats and hulls than in sunflowerseed and oat hulls do not have the same spongy lining as sunflower hulls. Hence, the effects noted for sunflowerseed are not as pronounced for oats. At the more intensive drying levels it was noted that the hulls tended to shrink so tightly onto the meats that they cracked or loosened. This probably accounts for the fact that at these drying levels the curves for percentage hulling of dried and undried seed coincide.

The definite and consistent lowering in the percentage of broken kernels is a reflection of an increased toughness or plastic quality in the meats. This effect is more noticeable for sunflowerseed since less drying of the meats occurred than in oats, and the high oil content of sunflower meats also imparts plasticity. On sharp impact this property causes the meats to break into two or three relatively large fragments as contrasted with the shattering effect that occurs at lower moisture levels.

It appears that with suitable adjustment of temperatures and drying times the moisture in the hulls of both sunflowerseed and oats can be materially reduced without changing the meat moisture appreciably. On hulling this

gives no material gain in percentage of seed hulled but can give a significant lessening of shattering damage to the meats. Thus the main advantage of flash drying is to simplify separation of meats and hulls.

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PACKAGING

VII. WATERPROOFING OF FIBREBOARD CONTAINERS[1]

By C. G. Lavers[2]

Abstract

An attempt was made to find a material in which domestic fibreboard cartons could be dipped to produce waterproof packages. The waterproofing agents tested included vinyl resins, cellulose acetates, nitrocelluloses, polystyrene, chlorinated rubber, corn protein – resin, a wood oil drier combination, an alkyd, and microcrystalline wax. Agents that did not coat the surface of the box, or gave only a very light coating, were not satisfactory. Wax could not stand rough handling at low temperatures. Two nitrocellulose formulations and one vinyl resin solution were found to be particularly suitable for this application. One of the nitrocellulose waterproofing agents dried at room conditions in 15 min., and boxes coated with it withstood water immersion for over 30 days after rough handling at −40° F. This method of producing waterproof packages appears to be quite practical.

Introduction

During the war, because of uncertain conditions of handling and warehousing, many tons of warlike stores had to be shipped in waterproof containers. One of the most common methods employed in making waterproof packages was by wrapping the product to be protected, either before or after placing it in a carton, in Grade *C* material (Cellophane laminated to scrim cloth and coated on both sides with microcrystalline wax), sealing by dipping in wax, and overwrapping with kraft paper to prevent packages from sticking together. This method was expensive, and labour and time consuming. Hence, it was felt desirable to attempt to find a material in which domestic fibreboard cartons could be dipped to produce a waterproof package that would require no further processing. Several commercial waxy and resinous products were tested for this application, and this paper presents the results.

With the cessation of hostilities and consequent improvement in shipping conditions, the need for waterproof packages was greatly reduced and hence this project was not continued. For this reason, the results presented are not as complete as they might otherwise have been; however, they do serve to indicate the performance that may be expected from various types of waterproofing agents and also show the practicability of this method of packaging.

Materials and Methods

It was believed that a material for the purpose described above should have as many of the following properties as possible. It should preferably be applied without heating; should dry rapidly; should require no overwrap

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to prevent packages from sticking together (blocking); should retain flexibility at low temperatures; and it should not soften and run off the package at high temperatures (140° F.).

The materials tested were of three general types: solvent deposited resins that left a surface film over the entire package, impregnating materials that left little or no surface coat, and wax. The agents tested included: vinyl resins, cellulose acetate, nitrocelluloses, polystyrene, chlorinated rubber, corn protein – resin, a wood oil drier combination, an alkyd, and microcrystalline wax. Further details are given in Table I.

An initial test of all samples was done as follows. Regular flat folding cartons with full overlapping long flaps (0.02 in. chip board; dimensions, $4 \times 2\frac{3}{4} \times 1\ 15/16$ in.; opening end, $2\frac{3}{4} \times 1\ 15/16$ in.) were filled with sawdust and closed with silicate glue. Seams around the top and bottom, and at the side, were sealed with a waterproof pressure sensitive tape, and the box was then dipped in the waterproofing agent under test, one-half at a time, allowing at least a $\frac{1}{2}$ in. overlap. Each material was tested both as a single and as a double coating. The waterproofing agents were allowed to dry at room temperature without forced draft for approximately the time indicated in Table I. The boxes were then immersed in water and left until failure, or for one month, whichever period was shorter.

Those materials that showed promise in the initial test were subjected to a rough handling test. Four cartons were given a single dip, and four a double dip in the medium. The packages were then placed in a wooden master container capable of holding 32 packages (two layers, each accommodating four by four cartons). The master container was a style two nailed wood box, constructed according to Canadian Packaging Committee Code No. 11.* The test packages were placed along the side of the box, and excess space in the centre was filled with dummy cartons containing sawdust. The loaded master container was stored at −40° F. overnight, followed by subjection to 20 free falls of three feet each (five falls on each long edge). Test packages were then removed from the wooden box, allowed to reach room temperature, and immersed in water.

As a further test of flexibility, the agents used in the rough handling test were subjected to a low temperature bend test. For this trial, strips of 50 lb. kraft (ream weights refer to 500 sheets, 24 × 36 in.) 1 in. by 8 in. were given single and double dips in the waterproofing medium, allowed to dry, stored at the temperature of test (−10° F. and −40° F.) for two hours, bent quickly (less than one second) around a $\frac{1}{2}$ in. diameter rod, and then examined for cracking or flaking.

An accelerated ageing test was also done on these materials. Single and double dipped packages were stored at 140° F. (low humidity, approximately 6%) for one month, and then subjected to water immersion.

* *Boxes, Wooden, Nailed. Can. Packaging Committee Code 11. Currently available from Forest Products Laboratories, Dept. of Mines and Resources, Ottawa, Canada.*

TABLE I

INITIAL TEST OF WATERPROOFING AGENTS

(Each result based on two packages)

Material	Approximate drying time, hr.	Results of water immersion, time (days) to failure with:	
		Single coat	Double coat
A. Vinylite resin in xylol, methyl ketone, and methyl isobutyl ketone	0.5	<1	<1
B. Vinyl resins in organic solvents containing added pigments and plasticizers	1.5	6	>30
C. Vinyl chloride acetate copolymer, high molecular weight, dissolved in acetone, plasticized	1.0	9	18
D. Vinyl resin emulsion plus solvents, plasticized	1.0	<1	<1
E. Vinyl resin emulsion plus solvents, plasticized	1.0	<1	<1
F. Vinyl and vinylidene resins in acetone and acetate solvents	1.5	>30	>30
G. Cellulose acetate dope	2.5	2	7
H. Cellulose acetate in acetone and other solvents, plasticized	18	2	16
Ia. Nitrocellulose, 21-22% non-volatile, in a solution of esters, alcohols, and hydrocarbons, plasticized	2.0	>30	>30
Ib. Nitrocellulose, 13% non-volatile, in a solution of esters, alcohols, and hydrocarbons, plasticized	2.0	>30	>30
J. Nitrocellulose in a mixture of ester solvents, plasticized	0.25	18	15
K. Styrene resin solution	2.0	<1	<1
L. Chlorinated rubber solution, plasticized	0.25	<1	<1
M. Corn protein – resin solution	1.0	<1	<1
N. Treated wood oil drier combination (leaves no surface film)	1.5	<1	<1
O. Alkyd, phthalic anhydride content 34% (on solid basis), linseed oil modified, petroleum spirit solvent	48	<1	<1
P. Microcrystalline wax: softening point, 150°-155° F.; penetration (100 gm. at 77° F.), 40-45; flexibility good, see Table III	1-2 Min.	<1	6

Since the shortest drying time possible would be desirable in the application of these materials, the drying time of the more promising samples was determined by a blocking test. Strips of 50 lb. kraft, 1 in. by 4 in., were dipped in the waterproofing material and allowed to dry under room conditions for a measured time. At the end of this time, four of these strips were placed on top of each other, and a 1 lb. weight was placed on top of the pile. The samples were stored at 120° F. overnight, then cooled to room temperature, and examined for blocking (sticking together). If blocking did not occur the drying time was reduced until samples just stuck together after this treatment.

Results

Waterproofing materials that left no surface coating on the box, such as *N* (Table I), failed to produce a watertight package because they did not seal the seams and corners of the boxes. Similarly agents that did leave a surface film but had very low viscosity failed to seal the seams because most of the waterproofing compound ran off the box before it had a chance to dry. Materials in this category were *A*, *L*, *O*, and probably *K*. The vinyl resin emulsions (*D*, *E*) were not satisfactory.

On the basis of the initial test for water resistance (Table I), nine of the materials appeared more promising than the rest and were selected for further study. These nine materials are listed in Tables II and III. The rough handling and ageing tests (Table II), indicated that waxes would not be suitable for this purpose if severe handling conditions were encountered. Agents *B*, *F*, *G*, and *H* were also severely affected by these tests. In addition materials *B*, *F*, and *H* all required over 15 hr. to dry (Table III), which further detracted from their value. It is possible that drying times might have been

TABLE II

ROUGH HANDLING AND AGEING TEST OF PACKAGES TREATED WITH WATERPROOFING AGENTS

(Each result based on four packages)

Material	Results of water immersion after rough handling Time (days) to failure with:		Results of water immersion after ageing Time (days) to failure with:	
	Single coat	Double coat	Single coat	Double coat
B	<1	<1	20	>30
C	20	>30	>30	>30
F	2	4	>30	>30
G	<1	10	6	10
H	<1	<1	8	8
Ia	<1	>30	>30	>30
Ib	<1	>30	>30	>30
J	>30	>30	>30	>30
P	<1	<1	<1	<1

TABLE III

FLEXIBILITY AND MINIMUM DRYING TIME OF WATERPROOFING AGENTS

Material	Temperature of bend test				Minimum drying time, hr.
	−10° F.		−40° F.		
	Single coat	Double coat	Single coat	Double coat	
B	Pass	Pass	Pass	Cracked	>15
C	Pass	Pass	Pass	Pass	1.0
F	Pass	Pass	Pass	Pass	>15
G	Pass	Pass	Pass	Pass	0.75
H	Pass	Pass	Pass	Cracked	>15
Ia	Pass	Pass	Pass	Pass	0.75
Ib	Pass	Pass	Pass	Pass	0.75
J	Pass	Pass	Pass	Pass	0.25
P	Pass	Pass	Pass	Cracked and flaked	—

reduced somewhat by using forced air circulation and heating devices, but under these conditions it was difficult to avoid the formation of bubbles in the coating when the solvent evaporated rapidly. The approximate drying time given in Table I does not always agree with that in Table III because the time shown in Table I is the time required for the material to be dry to the touch, whereas Table III gives the drying time required to eliminate blocking. Materials *J*, *C*, *Ia*, and *Ib* (the last two as double coats) appeared to be superior to the other agents and their relative merit fell in that order. It will be noted that all of these except *C* were nitrocellulose formulations, and *C* was a vinyl resin solution. However, it seems likely that some of the other materials tested such as chlorinated rubber, cellulose acetate, and polystyrene could have been improved considerably by changing their composition somewhat, i.e., by better plasticizing, or by increasing the viscosity either by increasing the non-volatile content of the solution or by using more highly polymerized resin.

The results indicate that this method of making waterproof packages would probably work quite satisfactorily using a waterproofing compound such as *J*, which required only 15 min. to dry under room conditions, and produced packages that withstood water immersion for over 30 days after rough handling at −40° F.

Acknowledgments

The author wishes to express his gratitude to Dr. J. A. Pearce of these laboratories for his kind advice, and to Mr. R. F. Plante for his technical assistance.

ANTIMONY TRICHLORIDE–ETHANOL PRECIPITATION FOR THE FLUOROMETRIC DETERMINATION OF RIBOFLAVIN IN PORK[1]

By Jessie R. Lewis[2] and Paul R. Gorham[3]

Abstract

A fluorometric method suitable for routine analyses is presented in which interfering substances in papain–takadiastase extracts of pork are precipitated in the presence of 0.02% antimony trichloride and 47.5% ethanol. Antimony trichloride prevents the adsorption of riboflavin upon the precipitate. Recoveries of 95 to 100% are obtained. Determinations by this method correlate well with those obtained microbiologically: for eight samples of fresh pork, four cooked, and four uncooked, $r = .94$; for 20 samples of cured pork, four cooked, and 16 uncooked, $r = .98$.

Introduction

The fluorometric determination of riboflavin in materials of low potency such as pork is made difficult by the relatively high proportion of pigments and other fluorescing substances that accompany riboflavin on extraction. Various techniques have been used, both singly and in combination, for minimizing the effect of these interfering substances: solvent extraction (6, 9, 13, 15, 26), adsorption and elution (1, 2, 3, 4, 10, 11, 12, 16, 21), precipitation (11, 13, 15, 23), permanganate oxidation (1, 2, 3, 5, 10, 11, 12, 16, 17, 18, 21, 24), and stannous chloride reduction (9, 15, 24). Usually, a correction must be applied for the fluorescence of non-riboflavin materials that still remain. Methods for destroying or quenching the fluorescence of riboflavin to obtain this correction factor include photolysis (7, 8, 21), reduction with sodium hyposulphite* (15, 17, 26), and treatment with strong alkali (19).

A proposed study of the effect of various curing methods on the retention of several of the B-complex vitamins in pork muscle required a rapid riboflavin assay that would give results in good agreement with those obtained by slower microbiological methods. The time-consuming adsorption and elution step frequently used for low-potency materials was avoided since complete adsorption of riboflavin from the extract is questionable (3, 16). Extensive trials of several existing methods (15, 19, 22, 23) gave unsatisfactory results. This led to the development of the following procedure, which utilizes a portion of the papain–takadiastase extract used for assaying other members of the B-complex.

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[2] *Laboratory Assistant.*

[3] *Biochemist, Food Investigations.*

* $Na_2S_2O_4 \cdot 2H_2O$, *often sold as sodium hydrosulphite, powdered.*

Procedure

Weigh into a 250 ml. centrifuge tube 5 to 15 gm. of minced sample and add 100 ml. of acetate buffer, pH 4.6, containing 0.4% of a mixture of equal parts of papain and takadiastase. Digest at 37° C. with constant agitation for 16 hr. Filter through Whatman No. 12 paper into a 200 ml. volumetric flask, adjust pH to 6.8 with 4 to 5 ml. *N* sodium hydroxide, and make up to volume.

Transfer a 25 ml. aliquot of this extract to a 100 ml. centrifuge tube. From automatic burettes add, with constant swirling, 1 ml. of 1% antimony trichloride in absolute ethanol followed by 24 ml. of 95% ethanol. Stopper the tubes, allow 15 min. for precipitation (preferably in the cold), and then centrifuge for five minutes at 2000 r.p.m.

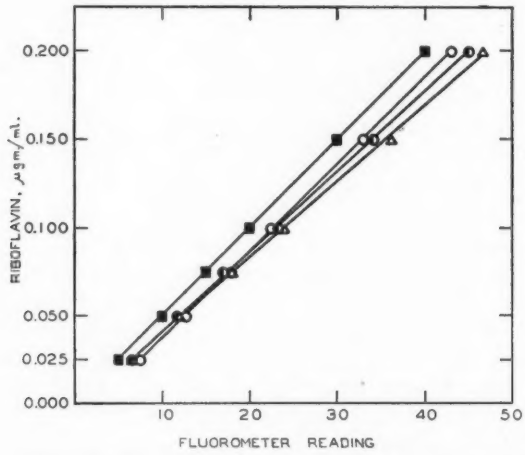

FIG. 1. *Riboflavin reference curves for various solvents. Water or 0.02% antimony trichloride in 47.5% ethanol* ■. *47.5% ethanol* ○, *23.75% ethanol* ◐, *50% acetone* △. *Each value is the mean of duplicate determinations.*

Take a 10 ml. aliquot of the supernatant liquid and determine its fluorescence with a Coleman No. 12 photofluorometer, using 0.1 μgm. per ml. sodium fluorescein to set the instrument at a reading of 50. Have all samples at room temperature when determining fluorescence. For the blank correction, add 0.25 ml. of a freshly prepared ice-cold solution containing 2 gm. sodium hyposulphite and 0.7 gm. of sodium bicarbonate in 20 ml. of water. Mix thoroughly, determine the residual fluorescence, and subtract this reading from that initially obtained. From an antimony trichloride – ethanol dilution curve (Fig. 1) convert this difference into concentration in micrograms per millilitre and multiply by the dilution factor to obtain the riboflavin content of the sample.

The importance of obtaining the blank correction with as little change in hydrogen ion concentration as possible needs to be emphasized. The use of strong alkali (19) to shift pH to 11 may largely destroy the fluorescence of riboflavin, but may equally well affect the fluorescence of the non-riboflavin materials being assessed. Moreover, with pork extract, it was found to create a turbidity that affected the precision of measurement. The use of 10 to 20 mgm. of solid sodium hyposulphite (4, 17) has been recommended, but addition by means of a solution is more convenient. Sodium hyposulphite readily decomposes in water, producing an acid solution that diminishes the fluorescence of non-riboflavin materials in pork extract. The recommended solution of sodium hyposulphite is stabilized somewhat by the sodium bicarbonate. It has a pH of 6.55, and the addition of 0.25 ml. to 10 ml. of extract at pH 6.8 does not alter the hydrogen ion concentration appreciably.

It should be noted that riboflavin in antimony trichloride – ethanol solution appears to the eye to have its yellow-green fluorescence masked by the blue fluorescence of the solvent. However, the sharp cutout of the filter transmitting fluorescent light, 90% transmission at 5400 Å to 0% at 5100 Å, excludes all measurement of the blue fluorescence (18).

Experimental

Initial attempts were made to clear extracts of cured pork by treatment with acetone or ethanol. Thirty-gram samples from eight different cures were extracted with papain–takadiastase, filtered, and each made to a volume of 200 ml. Aliquots of 25 ml. from six of the extracts were precipitated by an equal volume of acetone, and from four of the extracts by an equal volume of 95% ethanol. The solutions were filtered through Whatman No. 12 paper and the fluorescence of the filtrates was measured. Since riboflavin fluoresces more strongly in acetone or ethanol solution than it does in water (Fig. 1), the measurements were referred to dilution curves for the appropriate solvent in order to calculate the riboflavin content of the samples. Comparative microbiological determinations* were made upon the eight extracts. The results, expressed on a fresh-weight basis, are presented in Table I. The solvent precipitation and microbiological values were generally in poor agreement.

Significant losses of riboflavin occurred when small amounts of phosphotungstic acid, silver nitrate, copper hydroxide, or zinc hydroxide were added to pork extract treated with ethanol. The addition of 10 to 30 mgm. of antimony trichloride to 50 ml. of a mixture of equal parts of pork extract and 95% ethanol, however, appeared to improve clarification without causing loss of riboflavin.

Six uncooked (15 gm.) and three cooked (10 gm.) samples of cured pork were extracted and each made to a volume of 200 ml. Two aliquots of 20 ml. were taken from each extract. Five millilitres of water containing 5 μgm.

** All microbiological determinations were made by the method of Snell and Strong (25) modified by additions to the basal medium.*

TABLE I

COMPARATIVE RIBOFLAVIN ASSAYS OF CURED PORK BY THREE DIFFERENT METHODS, CALCULATED ON A FRESH-WEIGHT BASIS

Sample	Acetone precipitation			Ethanol precipitation			Microbiological
	Reading	Blank	μgm./gm.	Reading	Blank	μgm./gm.	μgm./gm.
1	28.5	8.0	1.1	—	—	—	1.6
2	37.0	9.5	1.5	—	—	—	1.9
3	53.5	7.5	2.6	—	—	—	4.0
4	45.0	7.5	2.1	—	—	—	3.2
5	25.5	6.5	1.1	25.5	4.5	1.2	2.0
6	30.0	7.5	1.3	32.0	6.5	1.5	2.5
7	—	—	—	55.0	10.0	2.8	3.7
8 (*a*)	—	—	—	20.5	1.5	2.2	3.6
8 (*b*)	—	—	—	19.5	1.5	2.1	3.6

of riboflavin was added to one aliquot and 5 ml. of water was added to the other. All samples were cleared by the addition of 1 ml. of 1% antimony trichloride in absolute ethanol followed by 24 ml. of 95% ethanol, and centrifuging at 2000 r.p.m. for five minutes. An aliquot of the supernatant solution was taken and its fluorescence determined. The amount of riboflavin in 20 ml. of extract was calculated from a reference curve for 0.02% antimony trichloride in 47.5% ethanol (Fig. 1). The fluorometer readings, blank corrections, amounts of riboflavin per aliquot, and percentage recovery are given in Table II. By repeatedly checking the photofluorometer against the fluorescein standard, and making all readings to the nearest 0.25 of a scale division, recoveries of 95 to 100% were obtained.

A somewhat different form of recovery experiment was performed upon an extract of fresh pork to compare the effects of clarification by ethanol, acid

TABLE II

RECOVERY OF RIBOFLAVIN ADDED TO EXTRACTS OF CURED PORK

Sample	Initial			5 μgm. added			Recovery, %
	Reading	Blank	μgm./20 ml.	Reading	Blank	μgm./20 ml.	
Uncooked:							
1 (*a*)	15.0	4.0	2.75	35.0	4.0	7.75	100
1 (*b*)	15.0	4.0	2.75	35.0	4.0	7.75	100
2	9.75	3.0	1.69	29.75	3.0	6.69	100
3	18.25	5.5	3.19	37.5	5.5	8.00	96
4	17.5	5.25	3.06	37.5	5.25	8.06	100
5	16.5	3.5	3.25	35.5	3.5	8.00	95
Cooked:							
5	20.25	5.5	3.69	40.25	5.5	8.69	100
6	15.5	6.0	2.38	35.5	6.0	7.38	100
7	20.25	8.5	2.94	40.25	8.5	7.94	100

ethanol, and antimony trichloride – ethanol. The extract from 90 gm. was adjusted to pH 6.75 and made to a volume of 1200 ml. The following amounts of riboflavin: 0, 1.25, 2.5, 3.75, 5.0, 7.5, and 10.0 μgm., each contained in 5 ml. of water, were added to 20 ml. aliquots of the extract. Twenty-five millilitres of 95% ethanol was added to each, and, after centrifuging, fluorometric readings were made. In a second series, 25 ml. of 95% ethanol made to pH 2.62 with a few drops of concentrated hydrochloric acid was used. A third series employed 1 ml. of 1% antimony trichloride in absolute ethanol and 24 ml. of 95% ethanol (in combination these have a pH of 2.62) for precipitation. The hydrogen ion concentration of each series of clarified extracts was determined. A reference curve for acid ethanol proved to be the same as the curve for water. In Table III, the riboflavin contents of the initial aliquots have been calculated from reference curves for the appropriate solvents. In the same way, increments in fluorescence caused by added

TABLE III

THE EFFECT OF THREE CLARIFICATION TREATMENTS UPON THE RECOVERY OF RIBOFLAVIN ADDED TO AN EXTRACT OF FRESH PORK

Treatment	Initial			Recovery, μgm./20 ml.						Average pH
				Added riboflavin						
	Reading	Blank	μgm./20 ml.	1.25	2.50	3.75	5.00	7.50	10.00	
Ethanol	15.5	3.5	2.40	1.00	2.25	3.25	4.70	7.10	9.65	6.90
Acid ethanol	15.5	3.0	3.13	1.25	2.50	3.75	5.00	7.50	10.00	6.75
Antimony trichloride – ethanol	15.0	3.0	3.00	1.25	2.50	3.75	5.30	7.50	10.00	6.65

riboflavin have been calculated as recovered riboflavin. Recoveries were lower and the blank was slightly higher with ethanol clarification than with the other two treatments. Ethanol somewhat decreased the hydrogen ion concentration as well.

Since the antimony trichloride – ethanol precipitates appeared more dense, a test was made to determine whether this treatment precipitated more material from the extract than did the acid ethanol or ethanol. This was done by means of nitrogen determinations since the reaction of antimony trichloride with water to precipitate antimony trioxide (20, p. 473) precluded weighing. The precipitates from the foregoing experiment were pooled by treatments. Each combined precipitate was washed twice with 47.5% ethanol, dispersed in water, and made to 50 ml. Duplicate micro-Kjeldahl determinations were run on each as well as on a sample of the unprecipitated extract. The amount of nitrogen precipitated from the enzyme-hydrolysed pork extract was not great. Antimony trichloride – ethanol precipitated 4.0%, acid ethanol 3.4%, and ethanol 3.2% of the total nitrogen in the extract.

The antimony trichloride – ethanol procedure was used for the determination of riboflavin in four samples of fresh and four samples of cooked pork. Sampling and analyses were carried out in duplicate and the results compared with microbiological determinations on the same extracts. The means of duplicate determinations by the two methods were highly correlated ($r = .94$), as illustrated by Fig. 2A. The standard error of a single determination was

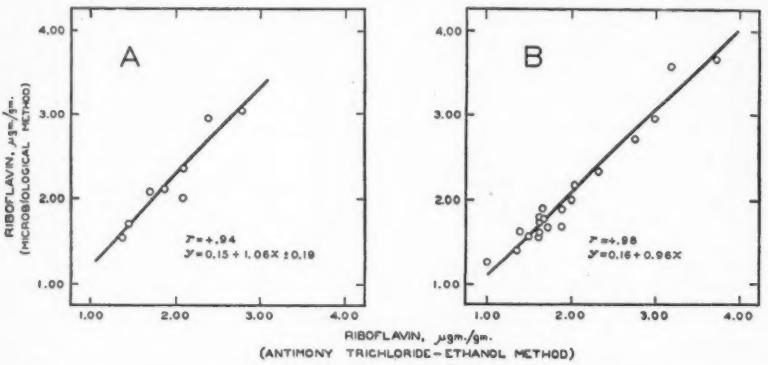

FIG. 2. *Correlations of riboflavin determinations by the antimony trichloride – ethanol and microbiological methods. All values calculated on fresh-weight basis.*

A. Means of duplicate determinations on fresh pork, uncooked and cooked.

B. Single determinations on cured pork, uncooked and cooked.

$\pm$ 0.16 μgm. per gm. for the fluorometric method and $\pm$ 0.08 for the microbiological method. The standard error of prediction of the microbiological value from the fluorometric value was $\pm$ 0.19 for the means of the two determinations, and was only slightly greater than the expectation from the variance of duplicates alone. Twenty samples of cured pork, four cooked and 16 uncooked, were extracted and single determinations of riboflavin were made by both microbiological and antimony trichloride – ethanol methods. The correlation coefficient for the determinations by the two methods was .98 (Fig. 2B).

Discussion and Conclusions

Acetone and ethanol both intensify the fluorescence of riboflavin, so that the linear relations with concentration are different from the relation for water or antimony trichloride – ethanol (Fig. 1). Antimony trichloride in contact with water forms hydrochloric acid and a bulky white precipitate, antimony trioxide (20, p. 473). It is this hydrochloric acid that decreases the fluorescence of riboflavin in ethanol for the same reference curve as that for water was obtained when a few drops of concentrated hydrochloric acid were substituted for the trichloride.

Solvent precipitation as a means of removing interfering substances has been noted as untrustworthy (15) because riboflavin may become adsorbed

on the precipitate. The fact that ethanol and acetone precipitation both gave results that were lower than those obtained microbiologically (Table I) tends to confirm this view. With antimony trichloride – ethanol precipitation, however, good agreement with microbiological assays (Fig. 2) and good recoveries of added riboflavin (Table II) were found. Low recoveries over a fairly wide range of concentration occurred when ethanol clarification was tested, but the addition of hydrochloric acid or antimony tricholoride to the ethanol resulted in almost perfect recoveries (Table III). This suggests that the presence of hydrochloric acid released by the antimony trichloride prevents the adsorption of riboflavin upon the precipitate.

It may be inferred from the good recoveries obtained using an external reference curve, that antimony trichloride – ethanol does not alter the fluorescence of riboflavin in pork extract. Therefore, an internal reference standard (6, 19, 22) with its more involved calculation is unnecessary. The external reference curve is so reproducible that routine calculations may be simplified further by multiplying the corrected readings by the factor 0.005 to convert them to concentrations in micrograms per millilitre.

In view of the high degree of correlation between microbiological and antimony trichloride – ethanol results, this method has been adopted by these laboratories for the routine assay of riboflavin in pork products.

Acknowledgment

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PRESERVATION OF EGGS

VI. EFFECT OF VARIOUS OILS AND OILING TEMPERATURES ON THE KEEPING QUALITY OF SHELL EGGS STORED AT 70° F. AND 30° F.[1]

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Abstract

The quality of eggs oiled when one day old with eight commercial oils and six mixtures and stored at 70° and 30° F. was assessed by candling, yolk index, and thick white height. Mineral oils with Saybolt viscosities of 70/100 at 100° F. maintained egg quality and prevented weight loss better than oils of lower viscosity. Viscosity of the oil seemed more important than pour point, although at 30° F. there was some indication that a high pour point was advantageous. Oiled eggs maintained their grades two to three times longer than unoiled eggs and lost from $\frac{1}{10}$ to $\frac{1}{4}$ as much weight. Heavy oil diluted with mineral spirits did not give as good results as lighter oils of comparable viscosity. The addition of vaseline and magnesium stearate improved the action of the light oils.

There was little difference in the quality of eggs dipped into oils maintained at 76°, 100°, and 130° F.

Introduction

In 1944 the British Ministry of Food requested the shipment of shell eggs to Britain and suggested that eggs placed in storage for shipment in the fall should be oiled. Although there are many reports on oils used for oiling eggs in the United States (e.g. 3, 6, 8, 9), little has been done in Canada. There is also some question as to whether the eggs should be oiled in cold or warm oil.* The present investigation was undertaken to determine which were the most suitable of the available oils and the effect of different temperatures of oiling.

Materials and Methods

The oils usually recommended for eggs are white mineral oils with low viscosities and high pour points. Oils of this type were obtained from a number of firms. Their characteristics as reported by the manufacturers, and as determined in these laboratories and by the N.R.C. oil testing laboratory, are given in Table I.

The main function of the oil is to seal the shell against water loss. The prevention of loss of carbon dioxide would also seem desirable so that the addition of substances more impervious to gas was indicated. Vaseline makes an excellent preservative but the thick films are messy and unsightly (7). In an attempt to seal the shell without the disadvantages of thick films one of the oils (*G*) was fortified with vaseline, or with magnesium stearate plus

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* *Shell Egg Committee of the Institute of American Poultry Industries. U.S. Egg & Poultry Mag. 48 : 302. 1942.*

TABLE I

PHYSICAL PROPERTIES OF OILS USED, ARRANGED IN ORDER OF DECREASING VISCOSITY

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Laboratory findings								
Viscosity, Saybolt								
Universal sec., 100° F.[1]	100	89	81		60	59	52	51
Sp. gr., 60° F./60° F.	.875	.850	.847		.833	.833	.833	.830
Pour point, °F.	5	15	10		45	45	30	35
Flash point (O.C.), °F.	375	385	370		340	340	320	320
U.S.P. acid test	Fail	Pass	Pass	Pass	Fail		Pass	Pass
Viscosity, S.U. sec., 76° F.	168	120	109	98	79		64	63
100° F.	101	87	82	69	60		52	51
130° F.	76	63	60	55	50		44	44
Manufacturers' specifications								
Sp. gr., 60° F./60° F.		.850/.860	.835/.845	.835/850	.825/.840		.820/.830	.825/.835
Viscosity, S.U. sec., 100° F.	77/82	85/90	70	70/80	50/60	50/60	50/60	50/55
Pour point, °F.	25	30	25	45	45	45	40	35
Flash point, °F.	355	345	310	345	325		300	280
Fire point, °F.	385	395	350	395	365			
Colour, Saybolt	30+	30+	30+	30+	30+		30+	30+

[1] *Calculated from centistokes.*

Nacconal. A heavy oil (350 viscosity) was diluted with an odourless kerosene in the proportions of 60 : 40 and 70 : 30. The viscosities of these mixtures are given in Table II.

TABLE II

SAYBOLT VISCOSITIES AT 76°, 100°, AND 130° F. OF THE OIL COMBINATIONS USED

		Viscosity at:		
		76° F.	100° F.	130° F.
I	350 oil + kerosene 70 : 30	102	76	55
J	350 oil + kerosene 60 : 40	72	55	45
K	Oil *G* + 7% vaseline	69	58	46
L	Oil *G* + 5% vaseline	68	53	45
M	Oil *G* + 0.2% magnesium stearate + 0.015% Nacconal	66	53	44
N	Oil *G* + 0.3% magnesium stearate + 0.015% Nacconal	64	52	44

The eggs were obtained from one producer who maintains a large, well managed flock of White Leghorns to which no new blood has been added for a number of years. The eggs were gathered in the morning, cooled for a few hours, packed in new Keyes trays and cases, and shipped so as to arrive at the laboratory the next morning. On receipt, they were candled, and cracked and off-grade eggs discarded. The eggs had not been cleaned and some had small spots of faecal contamination; the most noticeable of these were brushed off. The majority of the eggs were large but some of medium

size were distributed at random throughout the trays. Oiling was begun as soon as the eggs reached 50° F. to avoid surface moisture (dew point 45° F.). They were therefore oiled when one day old.

The oil was applied at the three temperatures commonly used; room temperature (in this case 76° F.), 100° F., and 130° F. The eggs were dipped nto the oil for a few seconds, drained for approximately two minutes, and returned to the original trays.

The eggs were weighed in tray lots of 30 eggs in a clean tray before oiling, and after oiling and draining overnight, to determine the amount of oil retained on the shell. They were also weighed in lots of six for determination of weight loss.

Two lots of eggs were received and oiled on successive days. Those used as controls were not broken out until the day after the others had been oiled, i.e. they were two days old. Two dozen were examined from each lot and the average of these was taken as the initial value.

The eggs were stored in wooden export cases at 70° F. (21° C.) (about 40% R.H.*) and at 30° F. (−1.1° C.) (about 55% R.H.). The eggs stored at 70° F. were examined after 4, 6, 8, 10, and 12 weeks; those at 30° F. were examined after 8, 16, 24, 32, and 40 weeks.

At each sampling, one dozen eggs were removed, candled, and broken out on a glass plate to check quality. Egg quality was assessed by candling, the height of the thick albumen (10), the yolk index (5), and the pH of the mixed thick and thin white. The pH was measured with a Beckman pH meter and the instrument was frequently checked with a standard 7.8 buffer.

Results

Effect of Oils

At both storage temperatures candling results showed that the most noticeable effect of oiling was the prevention of evaporation. Usually the range allowed in the size of the air cell corresponds to the yolk shadow standards found in each grade (2). However, in oiled eggs evaporation was so slow that yolk shadow was the only criterion by which grade could be really assessed. At 70° F. control eggs had large air cells (Grade *C*) in six weeks whereas all oiled eggs at 10 weeks had air cells $\frac{3}{16}$ in. or less in height (Grade *A*). With some oils this still held true at 12 weeks. By this time eggs treated with the poorest oils and mixtures graded *B* on air cell size. In spite of the slight amount of evaporation, the yolk shadows became more distinct on storage. Most of the controls were graded *C* on yolk shadow at six weeks, whereas most of the oiled eggs were graded *A* and *B*. After 10 weeks' storage, the controls were 'no grade' and the oiled eggs were practically all Grade *C* on the basis of yolk shadow. Of the 504 oiled eggs examined after 12 weeks' storage only nine were classed as no grade before the lamp.

* *R.H. = relative humidity.*

At the lower storage temperature the control eggs were graded *B* after 16 weeks' storage and *C* after 40 weeks. The majority of the oiled eggs were still Grade *A* after 32 weeks. At 40 weeks the air cells were on the border line between Grade *A* and *B* but based on yolk shadow most of the eggs were Grade *B*. Actually, of 504 eggs, 135 were graded as *A*, 362 as *B*, six as *C*, and one as no grade.

The value of oiling in maintaining quality at 70° F. is also apparent from the results presented in Table III. After 12 weeks the weight loss with the best oils (*A*, *B*, *C*, *D*) is $\frac{1}{10}$ or less of that of the unoiled controls while with the poorest oil it is $\frac{1}{4}$ of that of the controls. The yolk index (with the exception of Oil *G*) and white height after 12 weeks' storage is greater in the oiled eggs than in the controls after only four weeks' storage.

TABLE III

QUALITY TESTS ON OILED AND UNOILED EGGS AFTER 4 AND 12 WEEKS' STORAGE AT 70° F. AVERAGE VALUES PER EGG OVER THREE OILING TEMPERATURES. OILS ARRANGED IN ORDER OF DECREASING VISCOSITY

Oil	Weight loss, gm.		Yolk index		Thick white height, in.		pH	
	4 wk.	12 wk.	4 wk.	12 wk.	4 wk.	12 wk.	4 wk.	12 wk.
Unoiled[1]	3.64	11.80	.296	.174	.10	.08	9.29	9.30
A	0.29	1.00	.394	.346	.18	.16	8.36	8.20
B	0.38	0.87	.398	.357	.19	.15	8.32	8.30
C	0.41	0.81	.404	.352	.18	.16	8.30	8.25
D	0.22	1.05	.398	.348	.19	.18	8.35	8.30
E	0.27	1.24	.402	.343	.18	.16	8.40	8.48
F	0.40	1.14	.400	.339	.18	.15	8.34	8.39
G	0.41	2.70	.403	.281	.19	.12	8.43	9.24
H	0.48	1.90	.396	.305	.18	.14	8.46	8.60
I	0.26	1.25	.415	.333	.19	.14	8.31	8.32
J	0.66	2.66	.410	.288	.18	.12	8.59	8.82
K	0.38	1.44	.406	.336	.19	.16	8.40	8.64
L	0.40	1.46	.418	.337	.19	.15	8.36	8.62
M	0.39	1.56	.403	.339	.20	.16	8.33	8.44
N	0.34	1.38	.407	.341	.19	.15	8.28	8.54
Necessary difference[2]	0.14		0.020		0.017		0.21	

[1] *Original values—yolk index, .454; thick white height, 0.26 in.; pH 8.68.*

[2] *Necessary difference applies to oiled eggs only.*

The original pH value is high as the eggs were not examined until the day after the others had been oiled. The true original value is probably between this value and that given for the oiled eggs at four weeks. With the poor oils (*G* and *H*), carbon dioxide was apparently lost throughout the test and the pH increased with time. In all of the others there seemed to be a retention of carbon dioxide and the pH decreased until the 8th or 10th week of storage and then increased.

The analysis of variance of these results (Table IV) indicates that most of the variance due to oils can be attributed to the poor oils and mixtures (*G, H, J*). Much of the remaining variance is no doubt due to Mixture *I*. From the necessary differences (Table III) it will be seen that when the above four oils are removed there is no significant difference between yolk indices with any of the other oils and little of significance with white height. With weight loss and pH the oils fall into two groups, Oils *A, B, C,* and *D* giving better results than the other oils and mixtures.

TABLE IV

ANALYSIS OF VARIANCE ON DATA FOR OILED EGGS ONLY, STORED AT 70° F.

Source of variance	Degrees of freedom	Weight loss, mean square	Yolk index, mean square	White height, mean square	Degrees of freedom	pH, mean square
Oils	13				13	
G, H, J vs. others	1	158,383**	21,249**	122.67**	1	29,544**
Residual	12	4513**	289*	2.60*	12	679**
Temperature of oiling	2	409	286	0.18	1	1585**
Storage time	4	77,055**	33,894**	109.83**	4	3774**
Oils × temp.	26	616**	275*	3.84**	13	184
G, H, J vs. others × temperature	2	270	53	5.30	1	55
Residual	24	645	293	3.72	12	195
Time × oils	52				52	
G, H, J vs. others × time	4	11,923**	2722**	9.74**	4	1305**
Residual	48	836**	192	1.67	48	294**
Time × temp.	8	384	397*	0.58	4	279
Oils × time × temp.	104	301	156	1.13	52	113

**Exceeds 5% level of statistical significance.*
***Exceeds 1% level of statistical significance.*

Heavy oil diluted with mineral spirits did not give as good results as the lighter oils of comparable viscosity. The addition of vaseline and magnesium stearate improved the action of the light oil used but not to the level of the better oils.

The results of storing at 30° F. are with few exceptions much the same as at the higher temperature (Table V). With Oil *C* there was a greater loss in weight between the 32nd and 40th week than was expected. This was noticeable in each of the three lots of eggs oiled at different temperatures. Oils *D, E,* and *F,* which have high pour points, preserved quality better at this temperature than at 70° F. Oil *H* was also much better at the lower temperature.

As at the higher temperature, the weight loss with the oiled eggs was from $\frac{1}{10}$ to $\frac{1}{4}$ of that of the controls. In all but two instances the total loss over 40 weeks of storage was less in the oiled eggs than in the control eggs after eight weeks. The yolk index and white height of the oiled eggs at 40

TABLE V

QUALITY TESTS ON OILED AND UNOILED EGGS AFTER 8, 24, AND 40 WEEKS AT 30° F. AVERAGE VALUES PER EGG OVER THREE OILING TEMPERATURES. OILS ARRANGED IN ORDER OF DECREASING VISCOSITY

Oil	Weight loss, gm.			Yolk index			Thick white height, in.			pH		
	8 wk.	24 wk.	40 wk.	8 wk.	24 wk.	40 wk.	8 wk.	24 wk.	40 wk.	8 wk.	24 wk.	40 wk.
Unoiled[1]	1.46	4.27	7.20	.440	.404	.390	.21	.20	.20	8.86	8.88	9.01
A	0.07	0.43	0.71	.456	.449	.441	.22	.20	.21	8.12	8.06	8.29
B	0.23	0.42	0.77	.449	.457	.437	.23	.21	.20	8.00	8.04	8.30
C	0.22	0.50	1.11	.452	.439	.435	.23	.21	.20	8.14	8.10	8.25
D	0.14	0.55	0.95	.451	.451	.414	.23	.21	.21	7.98	7.98	8.56
E	0.21	0.47	0.84	.479	.444	.444	.24	.22	.22	8.24	7.98	8.22
F	0.18	0.44	0.77	.439		.431	.22	.20	.21	8.04	8.02	8.06
G	0.25	0.82	1.73	.442	.437	.407	.22	.20	.19	8.21	8.44	8.70
H	0.11	0.52	0.89	.456	.438	.450	.23	.20	.22	8.22	8.26	8.30
I	0.19	0.96	1.04	.457	.430	.413	.23	.21	.21	8.20	8.22	8.35
J	0.25	1.29	1.66	.447	.418	.416	.23	.19	.21	8.32	8.68	8.60
K	0.11	0.41	0.71	.442		.434	.23	.21	.23	8.12	8.22	8.21
L	0.18	0.42	0.90	.446	.453	.439	.23	.21	.23	8.11	8.19	8.32
M	0.19	0.45	1.04	.457	.444	.429	.24	.24	.23	8.14	7.96	8.46
N	0.13	0.56	0.84	.434	.444	.429	.23	.21	.21	8.02	8.24	8.38
Necessary difference[2]		0.17			0.016			0.02			0.16	

[1] *Original values—yolk index, .454; thick white height, 0.26 in.; pH 8.68.*
[2] *Necessary difference applies to oiled eggs only.*

weeks were as good as those of the unoiled eggs at 16 weeks. The final pH of all oiled eggs was much lower than that of the controls at eight weeks.

Effect of Oiling Temperature

During storage at 70° F. no significant effects of temperature of the oil at time of oiling could be found on white height, yolk index, or weight loss (Table IV). The pH was followed only in eggs oiled at 76° and 130° F.; eggs oiled at the lower temperature maintained a significantly lower pH throughout the storage period.

With eggs stored at 30° F. the temperature at which the oil was applied had no significant effect on weight loss, yolk index, or pH (Table VI). There was a significant effect with white height, the height being slightly lower in the eggs oiled at 76° F.

Amount of Oil Retained by the Eggs

The amount of oil retained by the eggs averaged from 1.0 to 2.4 gm. per tray of 30 eggs (each figure being the average of six trays), or 0.03 to 0.08 gm. of oil per egg. This is in agreement with Mallman's finding (6) of 0.06 to 0.07 gm. per egg. There was no apparent relation between amount of oil retained and the viscosity or temperature of the oil. It should be noted that these results were obtained after 24 hr. With the usual commercial equipment it has been found that it requires about twice as much oil having a viscosity of 70/90 as oil with a viscosity of 50/70. Warming the oil effects some saving.

TABLE VI

ANALYSIS OF VARIANCE ON OILED EGGS ONLY, STORED AT 30° F.

Sources of variance	Degrees of freedom	Weight loss, mean square	Yolk index, mean square	White height, mean square	Degrees of freedom	pH, mean square
Oils	13	6173.7**	666.8**	3.46**	13	1668.5**
Temp. of oiling	2	270.5	7.0	9.00**	1	236.0
Oils × temp.	26	160.2	152.9	1.65	13	71.2
Time	4	44,348.5**	3572.7**	26.50**	4	2622.0**
Oil × time	52	599.9**	271.5**	2.92**	52	286.5**
Temp. × time	8	130.2	131.0	3.63*	4	45.5
Oil × temp. × time	104	104.6	100.5	1.64	52	62.2

* *Exceeds 5% level of statistical significance.*
** *Exceeds 1% level of statistical significance.*

Discussion

The eggs used in this experiment were one day old when treated, which is said to be the ideal time for maintaining quality by oiling (4). The results indicate that oils with a Saybolt viscosity of 70 to 100 at 100° F. are more suitable for maintaining egg quality than the lighter oils. In general pour point was not as important as viscosity; at 30° F. however, a high pour point seemed to be of some advantage. The use of oil at temperatures higher than room temperature offered no advantage in preserving quality or in the amount of oil retained.

These findings are in the main in agreement with previous reports. Evans (3), using oils at about 70° F., found that those of higher viscosity preserved interior quality better than the less viscous ones. When applied at 239° F., oils with a viscosity of 134 Saybolt seconds were found to be more effective than those with a viscosity of 44 (1). Although in the present experiments the oils were used at much lower temperatures, the conclusions are similar. When a light oil was used, oiling at 60° F. was said to be better than oiling at 80° F. (9). The results presented here show that there was little difference between light and heavy oils applied over a much wider range of temperature. The use of oils at elevated temperatures seems to be a trade practice originating in a desire to save oil.

Although it seems reasonable that pour points above the storage temperature should give better results (8) the present work does not altogether support this claim. Some of the best oils had very low pour points according to the laboratory tests, and even according to the manufacturers' specifications the pour points were lower than the storage temperature. However oils with the same viscosity and different pour points were not available for comparison. Judging from the data presented in the above mentioned paper (8) there is an interrelation between viscosity and pour point.

Others (3) have noted that the reduction of the viscosity of an oil with solvents decreases its efficiency as an egg preservative; an oil having an original viscosity of 75 was diluted with 10% solvent to give a mixture with a viscosity of 58 to 62 Saybolt sec. at 100° F. The results were similar to those reported above (Table III, Oil *I*) when an oil with a viscosity of 350 was diluted to a final viscosity of 76.

Acknowledgments

The authors are indebted to the various companies for generous samples of oil, to Mr. D. B. W. Reid for statistical computations, and to the assistants who helped in various ways during the course of the experiment.

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DRIED WHOLE EGG POWDER

XXIV. SOME FACTORS AFFECTING COLOUR[1]

By H. Tessier,[2] J. R. Marier,[3] and Jesse A. Pearce[4]

Abstract

A nine filter colour comparator was used to compare egg powders with strips showing the colour of dried egg as received in the United Kingdom. Drying either fresh or frozen eggs did not affect powder colour but Grade *B* and Grade *C* eggs gave a product with a more intense yellow colour than Grade *A* eggs. The area of Canada in which eggs were produced did not affect the colour of the subsequent powder appreciably but powders prepared from eggs produced in May to July, 1945 were a more intense yellow than those from eggs produced in January to April of the same year. Exposure of the liquid egg to light before drying resulted in powders of a duller grey colour than when the liquid was kept in the darkness. Commercial cone-type driers gave powders of a more intense yellow than commercial box-type driers, while powders prepared on the laboratory drier were paler than those prepared on the commercial driers. Coarse powders scattered less of the impinging light than fine powders but the colour quality of the scattered light was unaffected. The addition of a mixture of two dyes, Tartrazine and Sunset Yellow, to liquid egg before drying improved the colour of the resulting powder.

Introduction

Dried whole egg powder shipped from Canada to the United Kingdom was usually considered to be of excellent quality. However, a general complaint was made about the pale yellow colour of the powder and about a pinkish tinge that appeared in some powders. These complaints arise from differences in colour preferences of the people in the two countries. In England, an egg with a dark yellow yolk is usually preferred, while Canadians usually like an egg with a pale yolk. This and Canadian economics have led to the use of diets for Canadian egg layers that will produce a pale yolk, hence the undesirably pale colour of Canadian egg powder.

Although work in these laboratories (4) and elsewhere (2) had described the darkening that occurred in egg powder during storage, there was little information about other factors that may affect powder colour. Some of these, examined in the present study, are: the type of drier, the time of year and area of the country in which the eggs were produced, the quality of the eggs, and exposure of the liquid egg to light. In addition, powders containing added colouring were examined.

The present paper describes colour measurements on variously treated powders using a nine filter comparator designed in these laboratories (5). Description of the results was facilitated by referring the measurements to a

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 187 of the Canadian Committee on Food Preservation and as N.R.C. No. 1512.

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[4] *Biochemist, Food Investigations.*

set of coloured strips depicting the colour of egg powders received in the United Kingdom and kindly supplied by the Low Temperature Research Station at Cambridge, England.

Materials and Methods

Since the studies described here were diverse in nature, descriptions of the materials used will be given in the various subsections of the results.

Both the brightness or intensity and the chroma or colour quality of the samples were measured by a nine colour method used earlier for meat (5) and eggs (4). By this method, colour quality was determined as the light scattered by the sample within any one of nine colour bands (5). The light scattered in any one band is expressed as a fraction of the total light scattered by the sample in relation to the light scattered by the standard white surface of magnesium carbonate. The brightness of the sample was determined as an item separate from the analysis of colour quality.

Wherever possible, the colour data were treated by statistical methods, and the values for factors having no significant differences were grouped, averaged, compared with colour data for the Low Temperature Research Station (L.T.R.S.) coloured strips, and are recorded here in terms of these strips.

Results

Colour Analysis of Low Temperature Research Station's Coloured Strips

The slides submitted were divided into four groups or series: P_1 to P_3 represented pale, pinkish-coloured egg powders characteristic of some of the powder produced in Canada; $2Y_1$ to $2Y_5$ showed shades of yellow, typical of the normal range of colour in American samples; Y_1 to Y_5 resembled the $2Y$ series, but had a greyish-yellow appearance, and represented egg powders that had lost their lustre as a result of overheating during the drying process or because of poor storage conditions; and the slides in the B group extended the Y series and showed badly burnt powders. In each group the members with lower numbers were of a paler shade than those with higher numbers.

The results of brightness measurements on the foregoing strips are given in detail in Table I. These data show that the P series scattered the greatest amount of the impinging light, i.e. they were the brightest, and the B series scattered the least. The greyish Y series scattered less light than the pink P group but slightly more than the normally coloured $2Y$ slides. Within the various series, the members with higher numbers scattered less light than the members with lower numbers.

The results of colour quality measurements on the various slides are also given in detail in Table I. However, since these detailed data are difficult to visualize, the colour quality profiles showing the averages of values for each group are presented in Fig. 1. These profiles show that the pinkish P series scattered more light in the blue and blue-green regions of the spectrum (385 to 525 mμ) than any of the other series and that the normally coloured $2Y$

TABLE I

COLOUR ANALYSES OF LOW TEMPERATURE RESEARCH STATION'S COLOURED STRIPS DEPICTING EGG POWDERS AS RECEIVED IN THE UNITED KINGDOM

Strip number	Brightness, %	Colour quality, % scatter								
		Blue			Green			Red		
		385-434 mμ	434-458 mμ	458-487 mμ	487-525 mμ	525-556 mμ	556-584 mμ	584-614 mμ	614-644 mμ	Above 644 mμ
P_1	66.2	4.8	10.5	11.5	18.7	13.2	21.3	9.6	5.7	5.7
P_2	62.4	4.9	10.7	11.4	17.4	13.2	21.2	9.7	5.8	5.7
P_3	62.0	5.0	10.5	11.5	17.3	13.0	20.9	9.9	6.0	5.9
$2Y_1$	56.6	4.8	7.5	9.4	16.1	14.4	24.8	10.7	6.2	6.1
$2Y_2$	56.5	4.4	7.2	9.4	15.6	14.5	25.4	10.9	6.4	6.2
$2Y_3$	51.4	3.9	6.6	9.7	14.5	14.3	26.3	11.4	6.7	6.6
$2Y_4$	49.7	3.8	6.0	9.0	14.3	14.3	27.0	11.8	6.9	6.9
$2Y_5$	45.0	3.1	5.9	9.0	14.1	14.2	27.5	12.1	7.1	7.0
Y_1	59.4	3.9	8.3	10.5	17.2	13.8	23.5	10.3	6.2	6.3
Y_2	59.2	3.9	8.4	10.6	16.8	14.1	23.5	10.3	6.2	6.2
Y_3	56.2	3.7	8.0	10.3	16.5	13.8	23.9	10.7	6.4	6.7
Y_4	52.2	3.8	7.7	10.1	15.7	13.8	24.0	11.0	6.7	7.2
Y_5	51.4	3.5	7.5	10.4	15.5	13.3	24.0	11.3	7.0	7.5
B_1	43.6	2.8	7.6	9.9	15.2	13.4	24.1	11.6	7.2	8.2
B_2	43.4	3.2	7.5	10.4	15.6	13.1	23.7	11.4	7.1	8.0

group scattered more light in the yellow region of the spectrum (525 to 584 mμ). The greyish-yellow Y series showed a slight increase in scatter in the red region (above 644 mμ) and the burnt B series showed a marked increase in this region. The foregoing differences were generally accentuated by changes within the series, from the palest to the most intense shades (Table I).

These preliminary measurements provided a quantitative basis for the examination of some of the factors believed to be responsible for the pinkish colour of some Canadian egg powder. However, measurements necessitated the inclusion of a hypothetical coloured strip, which, from the values reported here, would be lettered $2Y_0$.

The Effect of Particle Size on Egg Powder Colour

Differences in colour were observed for powders prepared in commercial driers and in the laboratory drier (6) and these were attributed in part to differences in particle size. To clarify this point, eight samples of commercially produced egg powders were screened for one hour on a Ro-Tap rotary sifter using sieves of 35, 65, 80, 100, 120, 200, and 325 mesh (U.S. Bureau of Standards) and each fraction of the samples was examined for colour. The average colour profile for all samples and all mesh sizes matched the profile of the yellow $2Y$ series and in particular the $2Y_1$ strip. The major difference was in brightness: the coarse fractions scattered less light than the fine fractions (Table II*A*).

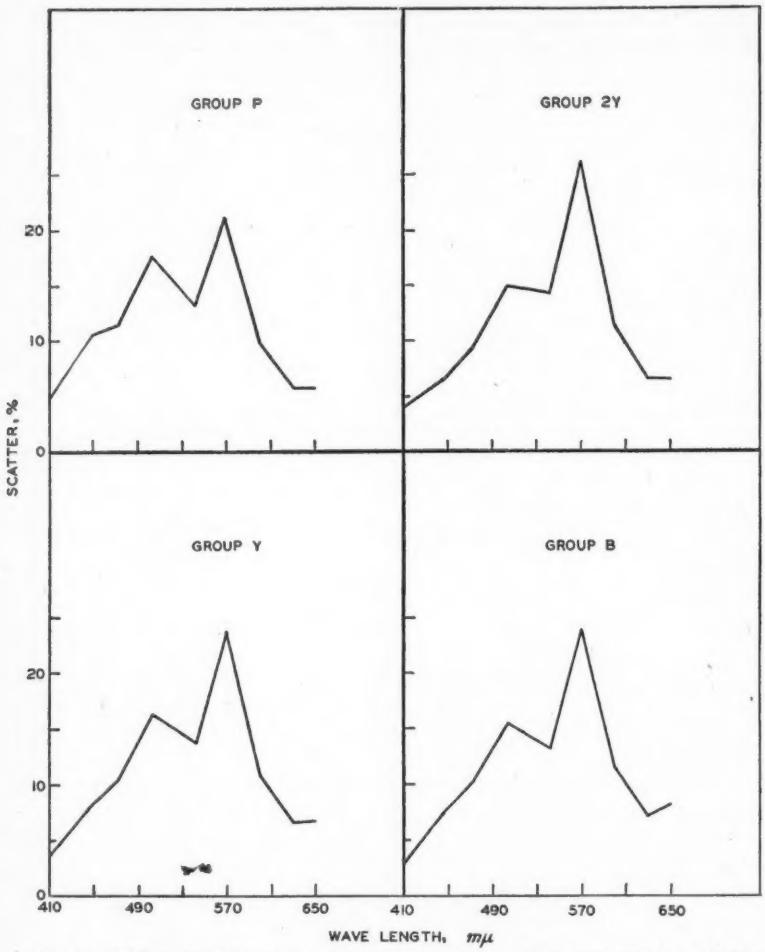

FIG. 1. *Colour quality profiles (averages) for the groups of coloured strips supplied by the Low Temperature Research Station, Cambridge, England.*

Sieving does not effect a complete separation of the particles of different sizes that are present in egg powder. Groups of particles may be seen in Fig. 2*e* at i, ii, and iii. These groups of particles do not break up during the sieving operation.

Further consideration was given to particle size and colour by the examination of powders prepared in a commercial cone-type drier using spray nozzles of different sizes: 0.065, 0.068, and 0.070 in. in diameter. The resulting powders matched the $2Y_1$ strip in colour distribution and, again, the finest powder (prepared using 0.065 in. nozzle) was the brightest (Table II*B*).

If the particle structure of egg powders is considered, explanation of the foregoing becomes apparent. Fig. 2 shows the microscopic structure of a number of samples. The particles passing a 35 mesh screen and retained by

TABLE II*A*

THE EFFECT OF PARTICLE FRACTIONATION BY SIEVING ON THE BRIGHTNESS OF EGG POWDERS

Particle range, U.S. Bureau Standards sizes	Brightness, % (average, eight samples)
35–65	49.1
65–80	52.1
80–100	51.8
100–200	53.3
200–325	55.9

TABLE II*B*

THE EFFECT OF SPRAY NOZZLE SIZE ON THE BRIGHTNESS AND PARTICLE SIZE OF EGG POWDERS PREPARED IN A CONE-TYPE COMMERCIAL DRIER

Nozzle diameter, in.	Brightness, %	Average particle size, mm.
0.065	56.0	0.03
0.068	54.2	0.05
0.070	51.5	0.4[1]

[1] *Size of clusters. Individual particles could not be measured.*

a 65 mesh screen are given for reference (Fig. 2*a*). These relatively large particles usually exude egg fat, which appears as smears (Fig. 2*a*) or discrete droplets (Fig. 2*f*). Powder from the main chamber usually consists of coarser particles than powder from the secondary chambers (Figs. 2*b*, 2*c*) and the difference between the main chamber and secondary chamber powder from cone-type driers is usually greater than the difference between the corresponding powders from the box-type driers.

The brightness differences recorded in Table II*B* are explained by Fig. 2 (*d*, *e*, *f*). Light is scattered from large particles in many directions and a relatively small proportion is reflected back to the light receptor (human or electric eye), while a powder made up of fine particles presents almost a plane surface and a greater amount of light is reflected in any one direction. From these considerations, and the data in Table I, fine powders should be paler in colour than coarse. The differences attributable to particle size would tend to weaken the comparison between brightness of powders and the brightness of the coloured strips. Nevertheless, it is believed necessary to give consideration to intensity measurements when transforming colour data to terms of the coloured stips.

Comparison of Canadian Egg Powder with L.T.R.S. Strips

It was thought desirable to determine how closely egg powder samples (commercial) could be matched with the various coloured strips by visual inspection, and opportunity was taken to determine whether the pinkish colour was attributable to the use of frozen liquid egg in the production of powder. As shown by the data in Table III, grading by visual examination gave a fairly good approximation of the results obtained by colour analysis. In addition, these results indicated that the use of frozen egg was not the sole cause of the pinkish powders.

TABLE III

COMPARISON OF METHODS OF CLASSIFYING EGG POWDER ACCORDING TO L.T.R.S. COLOURED STRIPS AND OF THE EFFECT OF THE PHYSICAL STATE OF THE EGG ON THE POWDER PRODUCED

Physical state of egg used to produce various powders	By colour analysis	By visual inspection
Shell eggs	$2Y_3$	$2Y_3$
Shell eggs	$2Y_0$[1]	P_1
Shell eggs	$2Y_2$	$2Y_2$
Shell eggs	$2Y_2$	$2Y_2$
Shell eggs	$2Y_2$	$2Y_1$
Mixed shell and frozen	P_3	P_2
Frozen melange	P_3	P_1
Frozen melange	P_3	P_3
Frozen melange	$2Y_3$	$2Y_2$
Frozen melange	$2Y_3$	$2Y_2$

[1] *This sample had the characteristics of the yellow 2Y series, but the values matched those of a hypothetical strip in this series that would be numbered* $2Y_0$.

Colour Characteristics of Powders Prepared in Canadian Plants During Various Periods of the Year

Samples of powder were taken from both the main drying chambers and from the secondary collectors of various Canadian egg-drying plants at monthly intervals during the months of June to November, 1943 and in March, 1944. At that time, it was possible to obtain powder from five cone-type driers and from four box-type driers. Two of the box-type driers were rectangular in shape with flat bottoms and the other two had V-shaped bottoms. In general, fresh or stored shell eggs were processed during June, July, and August, frozen melange during September, October, and November and fresh shell eggs in March, 1944.

The results (Table IV*A*) showed that on the average all powders collected from the main chambers of the various driers corresponded to the yellow 2*Y* group of slides and that the powders from the cone-type and V-bottom, box-type driers were more intensely coloured than the powders from the flat-bottom box. The powders from the secondary collectors of the cone-type drier were burnt more than the powders from the secondary collectors of the

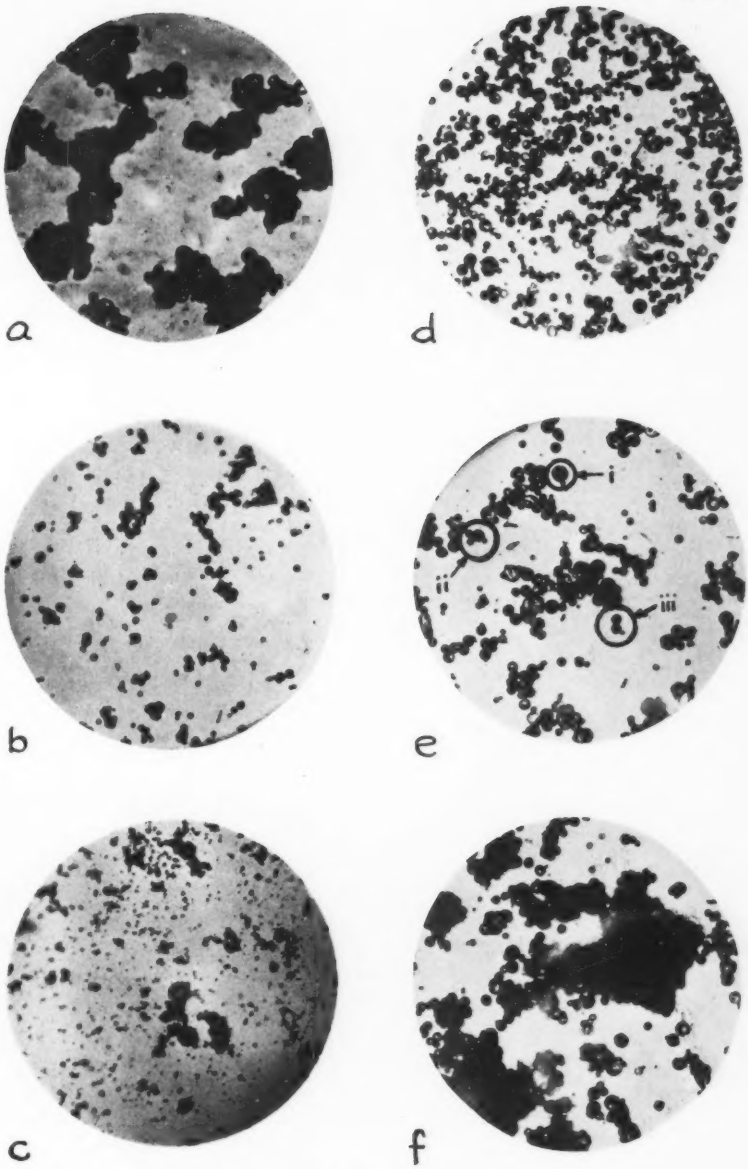

FIG. 2. *Photomicrographs of egg powder (× 37).*

(a). Fraction of a powder passing a 35 mesh screen and retained by a 65 mesh screen (U.S. Bureau of Standards).

(b). Powder from the main collector of a flat-bottomed, box-type drier.

(c). Powder from the secondary collector of a flat-bottomed, box-type drier.

(d), (e), and (f). Powders from the main collector of a cone-type drier, prepared using nozzles 0.065, 0.068, and 0.070 in. in diameter, respectively.

TABLE IV*A*

EFFECT OF DRIER TYPE AND COLLECTION CHAMBER ON THE COLOUR OF COMMERCIALLY PREPARED EGG POWDER

Type of driers	Number in operation	Grade according to L.T.R.S. coloured strips	
		Main chamber	Secondary collectors
Box, flat-bottom	2	$2Y_1$	Y_1
Box, V-bottom	2	$2Y_3$	Y_4
Cone	5	$2Y_4$	B_1

other two types. Since the powder caught in the secondary collector is finer than the powder trapped in the main chambers, it is reasonable to expect that these particles had dried faster and hence were more likely to be burnt.

Only the powder prepared in March, 1944 differed from the other powders (Table IV*B*). This supported previous evidence that the use of frozen egg had little effect on the colour of powder, but indicated that the time of year during which eggs are produced may have a pronounced effect.

TABLE IV*B*

EFFECT OF MONTH OF PRODUCTION ON THE COLOUR OF COMMERCIALLY PREPARED EGG POWDER COLLECTED FROM THE MAIN DRYING CHAMBERS OF NINE DRIERS

Month of production	Grade according to L.T.R.S. coloured strips
June to November, 1943	$2Y_3$
March, 1944	Y_3

Colour of Powders Prepared in a Laboratory Drier and in Commercial Driers

The survey of powders prepared in various commercial plants indicated that season of production of the eggs may be an important factor affecting the colour of egg powder. Information about this point could best be obtained by using the laboratory spray drier (6); therefore, a comparison was made of the differences in the colour of powder prepared in the laboratory drier and in commercial driers. For this purpose, two lots of frozen melange were used: a portion of one lot processed in western Canada was dried in a V-bottom, box-type drier and another portion in the laboratory drier; and a portion of the second lot processed in eastern Canada was dried in a cone-type drier and a portion in the laboratory drier.

As seen in Table V, the laboratory drier gave normally coloured powders ($2Y$ series) but these powders were a paler yellow than the powders from the commercial driers. This may have been a function of the scale of the laboratory and commercial operations: egg is dried in the laboratory drier at

lower temperatures than in commercial operations. In addition, this study indicated that the region of the country in which the eggs were produced might also affect the colour.

TABLE V

COLOUR OF EGG POWDERS PREPARED IN COMMERCIAL DRIERS AND IN A LABORATORY DRIER

Source of frozen melange	Type of drier	Grade according to L.T.R.S. coloured strips
Western Canada	Laboratory	$2Y_0$[1]
	Commercial, box-type, V-bottom	$2Y_1$
Eastern Canada	Laboratory	$2Y_1$
	Commercial, cone-type	$2Y_2$

[1] *See Table III.*

The Effect of Grade of Eggs and Locality and Month of Production on the Colour of the Resulting Powder

A comprehensive study was made of the effects of grade of eggs and the month and locality of egg production on the quality of the powder produced and these results have been reported (3). Colour measurements, made on the same material, are presented here. In brief, the experimental design required shipments of Grade *A** (large, medium, and pullet), Grade *B*, and Grade *C* eggs from Vancouver, Edmonton, Winnipeg, London, Belleville, and Three Rivers on the 15th of each month from December, 1944 to July, 1945. Upon receipt in the laboratory the various samples of eggs were dried in the laboratory drier, and therefore, all the colours recorded here are somewhat paler than would be obtained in a commercial drier.

The area of production had no significant effect on the colour of powder prepared from Grade *A* eggs; the averages of the colour measurements showed that eggs from all areas corresponded to the hypothetical colour strip $2Y_0$, i.e. a very pale powder of a normal yellow shade. It was not possible to get Grade *B* eggs from the Vancouver area, but a comparison for the other five areas showed that Grade *B* eggs from Edmonton, Winnipeg, and London gave powders corresponding to the yellow $2Y_2$ strip while a similar grade of eggs from Belleville and Three Rivers gave powders corresponding to the paler $2Y_1$ strip. In general, powders from Grade *B* eggs were a more intense yellow than powders from Grade *A* eggs. Unfortunately, insufficient Grade *C* eggs were received to make a valid comparison of these and Grades *A* and *B* eggs for the various areas.

When considering the effect of month of egg production, a marked difference was observed between powders prepared from eggs produced between January and April and those produced between May and July. The data for this

* *Descriptions of the various grades of eggs can be found in (1).*

period were, therefore, subjected to further mathematical analysis (Grade *C* eggs were included in these considerations). The results in Table VI show that eggs produced in the early part of the year, while still of a yellow colour, were much paler than eggs produced later in the year and Grade *C* eggs gave a more intensely coloured powder than Grade *B* eggs, which, in turn, were a more intense yellow than Grade *A* eggs.

TABLE VI

COLOUR OF POWDERS PREPARED FROM EGGS OF DIFFERENT QUALITY PRODUCED DURING JANUARY TO APRIL AND MAY TO JULY, 1946

Grade of eggs	Period of production	Grade according to L.T.R.S. coloured strips
A	Jan. to Apr.	$2Y_0$[1]
	May to July	$2Y_1$
B	Jan. to Apr.	$2Y_2$
	May to July	$2Y_4$
C	Jan. to Apr.	$2Y_2$
	May to July	$2Y_5$

[1] *See Table III.*

The differences attributable to grades of eggs can be explained on the basis of the Canadian grading system (1). When candled, the yolks of Grade *A* eggs must be barely discernible, the yolks of Grade *B* eggs can be somewhat darker, and the yolks of Grade *C* eggs can be distinctly visible and even mottled. The seasonal differences are probably a reflection of the onset of warm weather and the corresponding transfer of hens from buildings to out-of-doors.

Effect of Sunlight and Ultra-violet Light on the Colour of Egg Powder

The drying described in the previous section was usually done in a fairly well lighted laboratory. During the work, it was observed that samples prepared on a cloudy day were slightly different from samples prepared on a sunny day. Therefore, an examination was made of powders prepared from liquid egg exposed to sunlight or to an ultra-violet light (carbon arc) or from liquid held in total darkness. Powder prepared from liquid exposed to the ultra-violet light had the greyish tinge common to strips in the *Y* series and corresponded to strip Y_3 while powder from liquid exposed to sunlight corresponded to the normal yellow strips and matched $2Y_3$. Powder from liquid egg held in total darkness was unlike any of the L.T.R.S. strips. The colour quality of this powder when compared with the colour quality of the $2Y$ group (Fig. 1) showed greater scatter in the yellow region of the spectrum (556 to 584 mμ) and reduced scatter in the blue–green region (487 to 525 mμ).

This powder should represent a third group of strips of a more brilliant yellow than any forwarded from England and should be represented by a series called 3*Y*.

The Effect of Added Colouring Matter on the Colour of Egg Powder

Since alteration of the foregoing factors would effect little improvement in the colour of egg powder, it was thought possible that a more desirable looking dried egg powder might be prepared by the addition of various colouring materials. For this purpose, the dye combinations listed in Table VII were added in various amounts to liquid egg before drying in the laboratory spray-drier. Of these, none gave a powder with a colour profile similar to any of

TABLE VII

Dyes[1]	Proportions	Amounts, ml., added to one litre of liquid egg
Cheese colouring[2]	—	0.5, 1, 2, 4
Lemon pie colouring[3]	—	5, 10, 20
Tartrazine[4]	—	5, 10, 20
Tartrazine : Ponceau[4]	3 : 1	10
Tartrazine : Sunset Yellow[4]	3 : 1	10
Tartrazine : Sunset Yellow	7 : 1	5, 10
Tartrazine : Sunset Yellow	9 : 1	5

[1] *All but cheese colouring consisted of 5 gm. solid made up to 100 ml. with water: cheese colouring concentration was unknown.*

[2] *Kindly supplied by Chateau Cheese Co., Ottawa, Ont.*

[3] *Kindly supplied by Canadian Doughnut Co., Trenton, Ont.*

[4] *Kindly supplied by Dye and Chemical Co. of Canada, Ltd., Kingston, Ont.*

the series shown in Fig. 1, and many powders were so badly coloured that they were undesirable. Colours approximating the yellow 2*Y* series, by visual inspection, were obtained by the use of: 4 ml. of cheese colouring; 10 ml. of pie colouring (5% solution); or 5 ml. of a mixture of 9 parts Tartrazine and 1 part Sunset Yellow (5% solution) per litre of liquid egg. Considerations of cost and ease of handling led to the selection of the Tartrazine – Sunset Yellow mixture. By colour analysis, powders containing this dye scattered less light in the blue region of the spectrum (385 to 487 mμ), and more in the blue–green (487 to 525 mμ) and in the red (584 to 644 mμ) regions than the desirable yellow 2*Y* series. However, these powders met the visual requirements and commercial scale, trial shipments to the United Kingdom had a satisfactory colour.

Acknowledgments

The authors wish to express their thanks to Dr. J. W. Hopkins for statistical advice and to Mr. W. R. Coutts who made the statistical computations.

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DRIED WHOLE EGG POWDER

XXV. FURTHER STUDIES ON THE EFFECT OF ADDED SUBSTANCES[1]

By R. L. Hay,[2] Margaret Reid,[2] and Jesse A. Pearce[2]

Abstract

A number of substances added to liquid egg before drying had no effect on changes in palatability, fluorescence value, and total carotinoid pigment content of the subsequent powders when stored for 16 weeks at 80° F., for eight weeks at 100° F., or for four weeks at 120° F. Added soya lecithin did not increase the initial fluorescence, but egg lecithin did; added lecithin from either source did not accelerate fluorescence changes during storage. Measurement of vitamin A content in treated or untreated powder showed that loss of this component during four weeks' storage at 120° F. was less marked than during 16 weeks' storage at 80° and 100° F., but, at these lower temperatures, heated whole egg powder, heated dried white, heated dried yolk, and heated or unheated cystine or methionine had a preservative action. Suerose or sodium bicarbonate retarded vitamin A loss in stored dried yolk. Foaming volume measurements on freshly dried powders containing Nacconol S.N.F., Duponol, Roccal, and Aerosol showed that, in general, the addition of these wetting agents to liquid egg before drying adversely affected the aerating power of the powder. The addition of sucrose improved the baking quality of freshly prepared powders, the addition of lactose had a negligible effect and the addition of whey solids reduced the baking quality. When the powders were stored at 80° and 100° F. these three added substances had a preservative effect; sucrose being most effective and whey solids least effective.

Introduction

Dried egg deteriorates during storage even at moisture and temperature levels well below those currently in use by commercial egg drying establishments. As a result, several studies have appeared on the use of added substances in retarding deterioration (1, 9, 12, 15). Previous work in these laboratories showed that sucrose or sodium bicarbonate, when added to whole egg before drying, were effective in retarding loss in quality during subsequent storage (4, 12). Stored egg powder containing lactose has been found to have greater foaming power than a similar powder containing the same concentration of sucrose (2). The addition of 10% of spray-dried whey (containing about 70% lactose) to egg liquid prior to drying had the same protective effect as the addition of 10% lactose when the powders were stored at 117° F. (2).

Other substances likely to affect the keeping qualities of egg powder during drying and storage were indicated by work in related fields. Calcium acid phosphate and phenyl mercuric nitrate offered points of theoretical interest—the phosphate because of its use in baking, and the nitrate because it is believed to react with sulphur-containing compounds. If the sulphur-containing groups were involved in fluorescence development in egg powder,

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it was thought that their combination with a mercuric compound might prevent development of fluorescing substances. Lecithin, a component of egg commonly believed to be responsible for the development of off-flavours in many food products, may have been responsible for fluorescence increases in stored egg powder and thus warranted study. Since the previously noted (12) beneficial effect of sodium bicarbonate might be attributable to the presence of the carbonate ion, it was also believed advisable to ascertain whether carbon dioxide added before or during drying would retard fluorescence changes in stored powders.

During preliminary work (11) using a model spray drier (16) it had been observed that excessive heating during the drying operation seemed to prevent loss (oxidation) of vitamin A content in stored egg powder. Since this antioxidant action may have been caused by changes in the sulphur-containing amino acids, added cystine or methionine might prevent excessive loss of vitamin A in stored egg powder.

Reconstituted dried egg is seriously deficient in foaming power. It was believed that wetting agents, if their presence did not accelerate deterioration, might facilitate the reconstitution of egg powder and thus increase the foaming power.

The present paper amplifies some of the foregoing observations by describing: the changes in palatability and fluorescence of stored egg powders containing substances likely to affect deterioration of quality; the changes in vitamin A content of stored dried egg containing substances with possible antioxidant effect; the effect of wetting agents on the foaming power of egg powder; the changes in the baking quality of egg powders containing various amounts of sucrose, lactose, and whey; and the effects of sucrose or sodium bicarbonate on dried yolk or dried white.

Materials and Analytical Methods

All egg powders used in the investigation were prepared in a laboratory spray drier (16) at an inlet temperature of 250° F. and an outlet temperature of 140° F. and were adjusted to final moisture contents between 2 and 3%. Substances under study were added to the liquid egg before drying.

Palatability was assessed by a panel of 14 people, who tasted each sample as scrambled egg. The procedures used for reconstituting the powder and for scoring were the same as those described in an earlier publication (10).

A previously described procedure (10) for measuring fluorescence was used throughout, with the exception that a greater number of defatting operations was necessary to remove all the fat from the dried yolk.

The procedure used for measuring total carotinoid pigments provided a rough arbitrary evaluation of the amounts present in the powder (14). One gram of dried whole egg powder was weighed on an analytical balance to 5 mgm. The sample was transferred to a 250 ml. Erlenmeyer flask and 100 ml. of redistilled acetone was added. The flasks were corked tightly and

the mixture was gently swirled intermittently for 10 min. The mixture was then poured into an 18-cm. No. 12 Whatman folded filter paper and the filtrate collected in a narrow-necked glass vessel, which was tightly corked immediately and kept closed until needed. The transmission of this filtrate was measured, at 444 and 465 mμ on a Lumetron Colorimeter using matched square cuvettes. Redistilled acetone was used as the standard of 100% transmission.

Vitamin A estimation was done by a method outlined by Dann and Evelyn (3). The L values in Table V are for the total blue colour produced by each sample, no correction being applied for any remaining carotinoid pigments.

Foaming volume has been found suitable, with reservations, as a measure of the baking quality of egg powder (4, 7, 13). The foaming volumes of some unstored powders were determined by two procedures: in the first, 40.5 gm. of powder was mixed thoroughly with 75 ml. of distilled water and then beaten for 10 min. in a 'Mixmaster', set at No. 10 speed; the second eliminated the variable egg solids – added substances ratio, unavoidable in the first method, and maintained the egg solids in each determination at 19 gm. The foam was measured in a graduated cylinder. Foaming volumes of the stored powders containing added carbohydrates were measured using the first procedure.

The baking quality of some of the stored egg powders was also evaluated by measuring the volume of sponge cakes prepared by a procedure described in a previous publication (7).

Results

Effects of Added Substances on Changes in Quality and Carotinoid Pigments of Whole Egg Powder

This portion of the study evaluated the effect of materials added to the liquid egg before drying on changes in palatability, fluorescence, total carotinoid pigments, and vitamin A content of stored egg powder. The materials added and the concentrations used are given in Tables I and III. Carbon dioxide was added in unknown concentration but was introduced in two ways; in the first, the melange was saturated with the gas shortly before drying; in the second, the carbon dioxide was introduced into the drier during the drying process. The dried products were stored in tin-plate (air as headspace gas) for 16 weeks at 80° F., eight weeks at 100° F., and four weeks at 120° F. The times for this exploratory work were chosen on the basis of work described in earlier papers and permitted examination of the powders at about the point where they became unsuitable for use as an egg dish. Carotinoid and vitamin A determinations were not done on samples stored for eight weeks at 100° F. but were done on samples held for 16 weeks at this temperature.

As shown in Table I, the added substances used caused no significant change in the eating quality of fresh or stored whole egg powders as assessed by either fluorescence or palatability measurements.

The deteriorative changes in dried egg during storage may be due to the reaction of reducing sugar with amino acids (1, 6, 8). Sulphur-containing

TABLE I

EFFECT OF VARIOUS ADDED SUBSTANCES ON THE FLUORESCENCE AND PALATABILITY CHANGES IN STORED WHOLE EGG POWDER

Treatment of liquid whole egg	Fluorescence value				Palatability	
	Initial	80° F., 16 weeks	100° F., 8 weeks	120° F., 4 weeks	Initial	80° F., 16 weeks
Untreated	15.0	47.4	58.0	84.3	8.0	6.6
Liquid egg saturated with CO_2	13.2	40.1	60.1	86.0	8.0	6.6
CO_2 introduced into air in drier	12.0	47.1	65.0	85.0	7.7	6.0
Whole egg powder, 0.1%[1]	13.0	46.1	65.0	88.0	8.1	6.0
Dried white, 0.1%[1]	13.5	44.4	56.0	74.4	8.0	6.3
Dried yolk, 0.1%[1]	12.9	43.1	61.2	82.0	7.9	6.8
Cystine, 0.005%	14.4	46.0	59.2	81.4	8.1	6.6
Cystine, 0.005%[1]	12.1	43.1	55.3	76.0	8.5	6.0
Methionine, 0.005%	14.1	42.3	58.2	78.1	8.5	5.6
Methionine, 0.005%[1]	14.0	42.0	55.0	68.1	8.1	6.0
Nacconal S.N.F., 0.02%	15.1	41.0	59.3	86.1	7.6	7.0
Duponol, 0.02%	14.0	37.4	57.0	79.4	7.5	6.5
Phenyl mercuric nitrate, 0.08%	13.2	42.1	60.3	85.0	—	—
$CaHPO_4$, 0.2%	12.5	47.3	67.3	82.1	8.5	6.9

[1]*Heated for one hour in a vacuum oven at 212° F.*

amino acids may be involved in this reaction as it progresses in egg powder (6), however phenyl mercuric nitrate did not prevent their action nor did the addition of methionine or cystine increase the fluorescence values. This sugar–protein reaction produces some carbon dioxide (6). The beneficial effect of this gas or of the carbonate ion in preserving stored egg powders (9, 12) may, therefore, be explained by the law of mass action. The negligible effect of carbon dioxide in the present experiment is probably due to failure to attain a sufficiently high concentration in the powder.

The addition of lecithin as a possible cause of fluorescence development was given more detailed study. Commercially available egg and soya lecithin were compared by adding them to different lots of liquid egg at levels of 0, 0.01, 0.1, and 1.0%. In addition, some of each of the lecithins was heated for one hour in a vacuum oven at 212° F. before being added to different lots of liquid egg at the 1% level. The powders containing lecithin and a control sample were held at 80° and 100° F. and the fluorescence was determined initially and after one-, two-, three-, four-, and five-week periods. Since it was difficult to attain homogeneity in the liquid, the fluorescence values were more variable than usual. Therefore the data were subjected to an analysis of variance; the results are shown in Table II. As might be expected, both time and temperature had a significant effect on fluorescence development. From the results in Table II the necessary difference for significance* was calculated, and the samples that did not differ were grouped and averaged. The average values for the groups are given in Fig. 1. Neither heated nor

* *5% Level of statistical significance.*

TABLE II

ANALYSIS OF VARIANCE ON FLUORESCENCE DATA FROM A STORAGE EXPERIMENT ON EGG POWDERS WITH OR WITHOUT ADDED EGG LECITHIN OR SOYA LECITHIN

Variance attributable to:	Degrees of freedom	Mean square
Samples	8	254**
Temperature	1	4013**
Time	5	1674**
Samples × temperature	8	9
Samples × time	40	13
Temperature × time	5	280**
Residual (Error)	40	11

** *Surpasses 1% level of statistical significance.*

TABLE III*A*

EFFECT OF ADDED SUBSTANCES ON THE TOTAL CAROTINOID PIGMENTS OF STORED WHOLE EGG POWDER

Treatment of liquid whole egg	Transmission,[1] %							
	Filter 444 mμ				Filter 465 mμ			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks
Untreated	89.6	90.1	93.0	93.2	89.4	88.6	93.7	94.4
Whole egg powder, 0.1%[2]	84.7	88.3	93.0	89.7	87.0	85.2	91.0	91.5
Dried white, 0.1%[2]	81.1	82.2	86.5	86.0	82.4	81.8	82.2	90.3
Dried yolk, 0.1%[2]	75.3	74.5	82.5	84.4	76.8	79.1	81.1	86.6
Cystine, 0.005%	82.3	81.6	85.2	85.6	81.3	83.1	87.0	90.5
Cystine, 0.005%[2]	73.0	74.6	81.4	82.0	74.5	76.6	82.4	84.7
Methionine, 0.005%	76.0	76.9	81.6	81.5	77.4	77.8	84.3	85.6
Methionine, 0.005%[2]	81.5	74.4	82.2	89.3	82.5	82.3	85.2	90.3

TABLE III*B*

EFFECT OF VARIOUS SUBSTANCES ON THE VITAMIN A CONTENT OF STORED WHOLE EGG POWDER

Treatment of liquid whole egg	L value[3]			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks
Untreated	20.2	10.6	7.9	22.4
Whole egg powder, 0.1%[2]	17.8	14.1	10.6	14.7
Dried white, 0.1%[2]	22.4	16.7	18.7	17.5
Dried yolk, 0.1%[2]	17.4	16.4	18.7	17.5
Cystine, 0.005%	19.3	14.1	13.8	18.2
Cystine, 0.005%[2]	19.9	16.0	14.9	19.2
Methionine, 0.005%	16.3	18.7	10.6	17.8
Methionine, 0.005%[2]	18.8	13.8	12.0	16.2

[1] *Varies inversely as the carotinoid pigment content.*

[2] *Heated for one hour in a vacuum oven at 212° F.*

[3] *Varies directly as the vitamin A content.*

unheated soya lecithin affected the initial fluorescence value of the powder but unheated egg lecithin caused a slight increase and heated egg lecithin caused a marked increase in the initial fluorescence value. However, the addition of lecithin did not accelerate fluorescence development during storage.

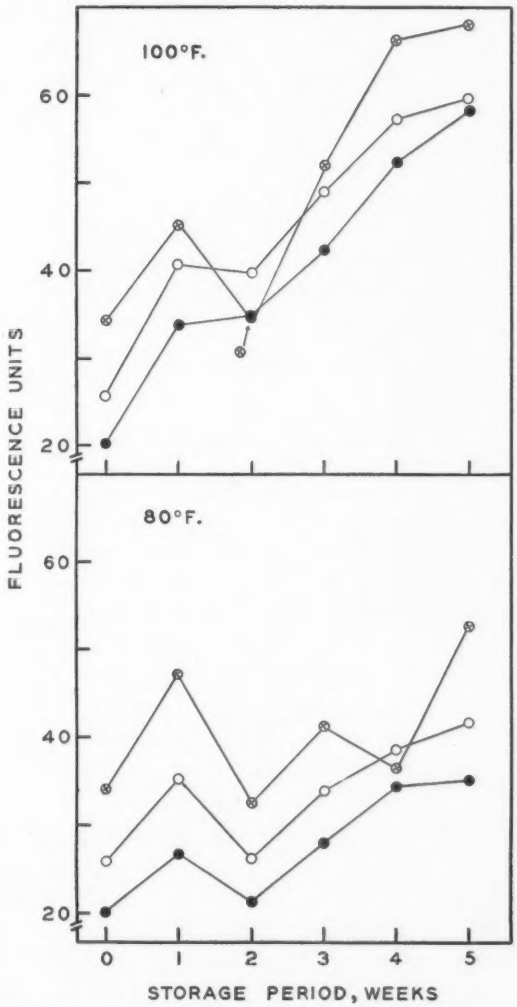

FIG. 1. *The effect of added heated or unheated egg or soya lecithin on the fluorescence changes in stored egg powder.*

● *Control powders and powders containing heated or unheated soya lecithin.*
○ *Powders containing unheated egg lecithin.*
⊕ *Powders containing heated egg lecithin.*

The results in Table III*A*, based on transmission values that vary inversely as the carotinoid content, show that most of the materials, studied primarily for their antioxidant effect, had no significant effect on changes in total carotinoid pigments. This may be partly attributable to wide variation in carotinoid pigments in the freshly prepared powders. Little change occurred during 16 weeks at 80° F. but reduction in carotinoid pigment was noticeable in all samples after 16 weeks at 100° F. and after four weeks at 120° F.

As shown in Table III*B*, all of the addition substances examined in this phase of the investigation (heated whole egg powder, heated dried white, heated dried yolk, and heated or unheated cystine or methionine) had a beneficial effect on vitamin A retention during storage at 80° and 100° F. No significant reduction in vitamin A content was observed in treated or untreated whole egg after four weeks at 120° F. After 16 weeks at 80° or 100° F. the loss of vitamin A was considerable. Previous work showed that loss of vitamin A was pronounced at all storage temperatures from 15° to 100° F. (5).

Effects of Sodium Bicarbonate and Sucrose on Changes in Dried Egg White and Dried Egg Yolk

Further information about the manner in which sucrose or sodium bicarbonate exert a beneficial effect on whole egg was sought by examination of dried white and dried yolk containing these substances. Sodium bicarbonate effectively retarded fluorescence changes in egg white stored at 120° F. and accelerated fluorescence development at 80° and 100° F. (Table IV*A*). This compound was mildly effective in inhibiting fluorescence development in yolk stored at 100° and 120° F. but had no effect at 80° F. Sucrose accelerated deterioration in yolk but had no determinable effect on the white. These and former observations (12) indicate that bicarbonate is most effective in retarding fluorescence development at high storage temperatures. From the data in Table IV*A* and previous work (2, 12) it appears that sucrose is not an effective preservative of eating quality unless used in dried whole egg. These problems are receiving further attention in the laboratories.

As shown in Table IV*B*, the presence of sodium bicarbonate had no effect on total carotinoid pigments in dried yolk. The large quantity of added sucrose diluted the carotinoid pigment content as measured but also appeared to reduce the change during storage. Loss in vitamin A content of yolk was marked under all conditions of study but reduction was retarded noticeably by the presence of sucrose (Table IV*C*).

Effects of Added Wetting Agents on Foaming Volume of Whole Egg Powder

Since wetting agents did not accelerate deterioration, their effect on the foaming power of reconstituted egg was evaluated by adding the following to the melange prior to drying: Nacconol S.N.F., Duponol, Roccal, and Aerosol.

TABLE IV

EFFECT OF SODIUM BICARBONATE AND SUCROSE ON CHANGES IN STORED DRIED WHITE AND STORED DRIED YOLK

A. Fluorescence value

Treatment of liquid white or yolk	Fluorescence value			
	Initial	80° F., 16 weeks	100° F., 8 weeks	120° F., 4 weeks
White				
Untreated	8.0	41.1	68.0	165.0
Sodium bicarbonate, 0.2%	8.0	66.1	164.0	46.0
Sucrose, 15%	11.7	40.0	86.0	158.0
Yolk				
Untreated	15.0	52.2	57.0	54.0
Sodium bicarbonate, 0.2%	14.0	56.0	48.1	43.0
Sucrose, 15%	10.5	64.0	97.2	165.0

B. Carotinoid content

Treatment of liquid yolk	Transmission, %							
	Filter 444 mμ				Filter 465 mμ			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks	Initial	80° F., 16 weeks	100° F., 16 weeks	120° F., 4 weeks
Untreated	80.1	80.0	86.0	87.0	81.5	81.2	87.1	89.6
Sodium bicarbonate, 0.2%	80.1	82.1	83.5	88.0	81.5	81.0	88.7	90.2
Sucrose, 15%	95.1	95.5	96.8	98.0	95.5	94.5	97.8	99.7

C. Vitamin A content

Treatment of liquid yolk	L value			
	Initial	80° F., 16 weeks	100° F., 16 weeks	120°F., 4 weeks
Untreated	30.7	18.7	18.7	19.2
Sodium bicarbonate, 0.2%	26.2	21.1	14.9	18.7
Sucrose, 15%	22.4	20.3	16.4	21.4

Table V shows that the presence of wetting agents usually had an adverse effect on the foaming volume of plain egg powder. Although powders containing 0.01, 0.02, or 0.04% Duponol had higher foaming volumes than plain

egg powder, similar amounts of added Nacconol, Roccal, and Aerosol had either a negligible or a detrimental effect. For all powders containing higher quantities of wetting agents the foaming volumes were lower than for untreated powders.

TABLE V

EFFECT OF ADDITION OF WETTING AGENTS ON FOAMING VOLUME OF WHOLE EGG POWDER

Concentration of wetting agent, %	Foaming volume, ml.			
	Nacconol	Duponol	Roccal	Aerosol
0	323	323	323	323
0.01	324	356	314	326
0.02	312	368	321	330
0.04	279	349	303	322
0.08	286	264	301	310
0.20	269	298	298	272
0.50	271	258	279	263

Effects of Added Sucrose, Lactose, and Whey on Foaming Volume and Baking Quality

Samples of egg powder containing 0, 3, 6, 9, 12, 15, or 18% sucrose, lactose, or whey solids were prepared. Some samples were examined for foaming power and baking quality before storage while others were sealed in air and stored at 80° and 100° F. Samples were examined by foaming volume only after four weeks' storage at 80° F. and after two weeks' storage at 100° F. At about this time, it became apparent that foaming volume was not a satisfactory measure of baking quality and the final testing, after 12 weeks' storage at 80° F. and eight weeks at 100° F. was for baking volume only.

Two procedures for foaming volume were used since it was difficult to add either carbohydrate or egg in such a way that all components would have identical prior treatment. The results obtained using both foaming volume procedures were similar in nature and are presented graphically in Fig. 2. In subsequent work only the procedure based on a constant amount of total solids in the mix was used.

Fig. 2 shows that the higher quantities of added sucrose resulted in a product with much greater foaming volume than that of untreated powders. Large quantities of lactose had practically no effect and large quantities of whey solids affected foaming volume adversely. It was also noted that powders containing 12% or more whey solids had an offensive odour that might prove harmful to the palatability of baked products.

Results after storage (Fig. 3) showed that, in addition to having the best initial foaming volumes, sucrose treated powders were most stable in this attribute during storage at 80° and 100° F. for four and two weeks respectively. Further examination by baking volume measurements (Fig. 3) also showed the marked beneficial effect of added sucrose on the baking quality of fresh and stored powders. Contrary to the results observed with the foaming

Page 168, first line of paragraph under subheading under Table V, for "0,3,6,9,12,15, or 18%" read "0,10,20,25,30,35, or 40%".

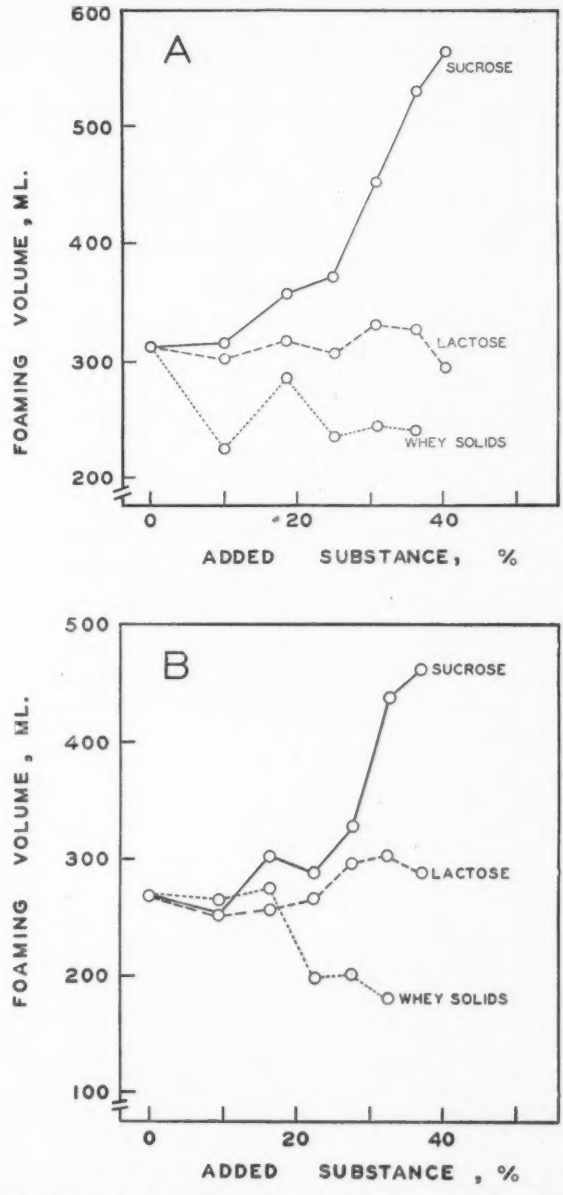

FIG. 2. *The effect of added sucrose, lactose, and whey solids on the foaming volume of egg powder; A, total solids in the mix are kept constant; B, egg solids in the mix are kept constant.*

volumes, lactose improved the baking quality of the fresh powders and provided some protection to stored powders. Added whey had an adverse effect on the baking volume of freshly prepared powder but retarded changes in the stored powders.

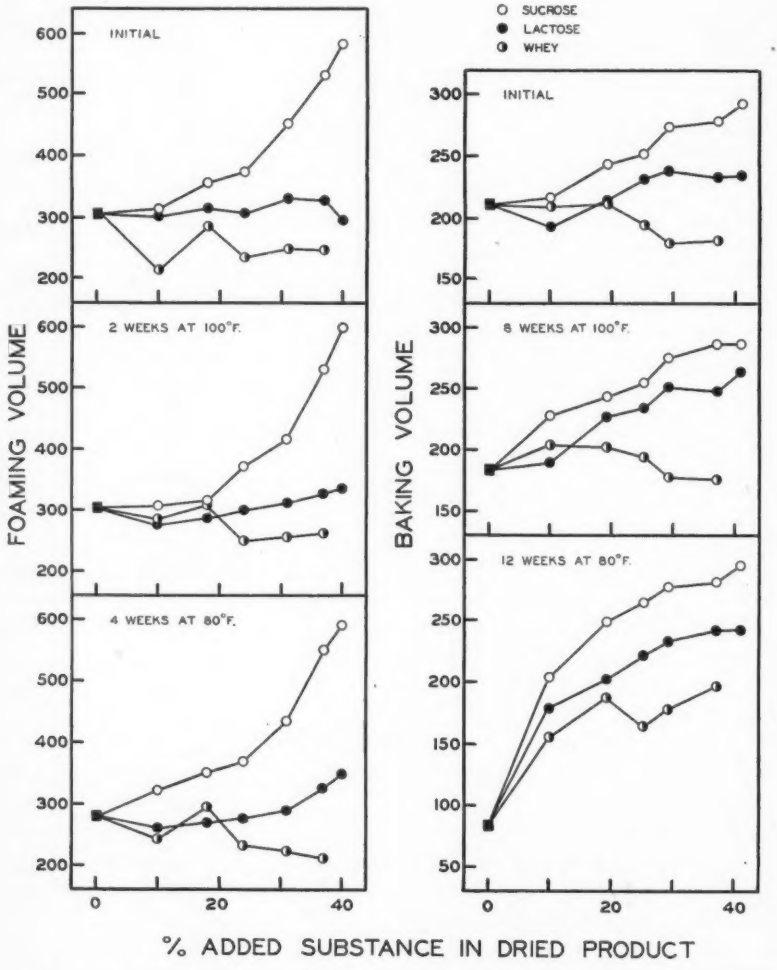

FIG. 3. *The effect of added sucrose, lactose, and whey solids on the foaming volume (total solids in the mix are kept constant) and baking quality of stored egg powder.*

The marked protective action (in terms of aerating power) provided by sucrose, a non-reducing sugar, and the lesser protective action of lactose, a reducing sugar, when considered in relation to the sugar–protein reaction is

at present unexplainable. This is receiving further attention in these laboratories.

Foaming Volume and Baking Quality of Mixtures of Dried Whole Egg and Dried Whey

To test the effect on foaming volume of whey added to whole egg powder, 0, 10, 20, 30, or 40 gm. of dried British or Canadian whey solids was mixed with 19 gm. of plain egg powder, 56 ml. of water was added, and the mixture was beaten and measured in the usual manner. The resulting foaming volumes, given in Table VI*A*, indicated that sponge cakes prepared from egg powder with part of the sucrose replaced by whey would be lower in volume than cakes produced from dried egg and sucrose.

TABLE VI

FOAMING VOLUME AND BAKING QUALITY OF MIXTURES OF DRIED WHOLE EGG AND DRIED WHEY

A. Foaming volume

Amount (gm.) of dried whey added to 19 gm. of whole egg powder	Foaming volume, ml.	
	Canadian dried whey	British dried whey
0	186	180
10	160	148
20	154	114
30	137	104
40	121	101

B. Baking quality

Weight (gm.) of sugar in baking formula replaced by British dried whey	Baking volume, ml.
0	209
1	210
3	182
7	126
15	93

To verify this, 0, 1, 3, 7, or 15 gm. of spray-dried British whey was mixed with 6 gm. of plain egg powder and sucrose was added to make the whey and sucrose for each determination total 20 gm. The solids were mixed thoroughly with 19 ml. of tap water, followed by beating for 10 min. in a 'Mixmaster' set at No. 10 speed. Then 20 gm. of standardized super cake flour was incorporated with the least amount of mixing. The remaining portion of the baking procedure used here was the same as that described previously (7). The volumes of sponge cakes made using these mixtures are given in Table

VI*B* and confirmed the above indication that the volume of sponge cakes prepared by substituting dried whey for sucrose decreased as the amount of added whey increased.

Acknowledgments

The authors wish to express their thanks to Canadian Industries Limited who kindly supplied the Duponol used in this investigation, to Miss S. Jegard, Biochemist, who measured the baking volumes, and to Messrs. H. Tessier and G. A. Young, Laboratory Stewards, for their valuable technical assistance.

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DRIED WHOLE EGG POWDER

XXVI. SOME OBSERVATIONS ON THE QUALITY OF POWDER PREPARED FROM FROZEN, LIQUID EGG[1]

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Abstract

Liquid from eggs of various qualities was frozen at −40° F. and stored at 10°, 0°, and −10° F. for 12 months. Powder produced from the defrosted samples was assessed by fluorescence and potassium chloride solution solubility measurements, which showed that liquid from musty or incubator reject eggs gave a less desirable powder than liquid from Grade *A*, Grade *C*, or cracked eggs; increase in time of frozen storage decreased the quality of the resulting powder; if frozen storage extended beyond six months, the lowest storage temperature was most desirable; and method of packaging (in Reynold's Metal A-10, or in wax paper with or without added ice) had no effect on the quality of the powder produced. If drying conditions were held constant, increased dilution of the defrosted egg before drying resulted in a poorer powder. It was shown that freezing or defrosting operations should be completed within about one hour.

Introduction

At the time these studies were planned, it was apparent that large quantities of the eggs produced in the spring and summer in Canada and used for subsequent drying would have to be stored. The capacity of the drying equipment available was not sufficient to process during the flush season the total amount of powder required for export, nor even to process the eggs within the time they might reasonably be stored in the shell. Eggs in the shell should be held for no longer than about three months and conditions required that they be held for six to eight months. This long term holding is usually done by breaking the eggs, mixing the white and yolk, and freezing the resulting liquid. However, little information was available to describe the effects of frozen storage of liquid egg on the quality of the resulting powder. This paper describes the results of quality measurements on powder produced from frozen liquid egg.

Materials and Methods

The material used in the preliminary study was prepared from the meats of Grade *A* large, fresh eggs. For this study, 700 ml. aliquots of egg were frozen into blocks 5 × 7 × 1.5 in. at −40° F. The blocks were lashed together in sets of four, separated by wooden strips so that each block had an equal area of surface exposed. The sets were stored unwrapped for 18 months at 0° and 15° F.: some exposed to the air in the storage rooms; others in closed

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desiccators containing 50% and 20% sulphuric acid. Initially, the acid solutions should have given relative humidities of 35% and 87%, but these values no doubt changed slightly until equilibrium was reached.

The later more comprehensive storage study utilized material described in earlier papers (2, 5). In brief, liquid from fresh Grade *A* eggs, from Grade *A* eggs held for 16 hr. at 80° F. in sterile glass containers, from Grade *C* eggs, from cracked eggs, from musty eggs, and from 'eight-day' incubator reject eggs was poured into moulds containing about four litres, frozen within 16 hr. in a room operating at −40° F., and held at temperatures of 10° (+ 2°, − ½°), 0° (± 1°) and −10° (± 1°) F. for a period of one year. Samples were dried before and after freezing and after 3, 6, and 12 months' storage. The liquid from fresh Grade *A* eggs was packed in Reynold's Metal A-10, a highly moisture vapour resistant material (8), plus a Fourdrinier Kraft, B-Flute carton; in wax paper (40 lb. Kraft, waxed to 50 lb.) plus the carton, with ice cubes inside the carton and surrounding the wrapped egg; and in wax paper and carton without added ice. All the other samples were packed in Reynold's Metal A-10 and cartons.

Accessory studies on material prepared from the meats of Grade *A* large, fresh eggs included evaluation of the effects of dilution of the defrosted egg, freezing rates, and defrosting rates. The freezing time was considered as the time for the centre of the block to reach a temperature of −20° F. At this temperature approximately 7% of the melange is still unfrozen (6).

The egg was dried in a laboratory spray drier (10), and for all but the freshly frozen material, the inlet and outlet temperatures were 250° and 140° F. respectively. Dilution of defrosted egg is usually desirable if the viscosity of the material is to be reduced to a point where the egg can be handled by the pump on the drier and was a necessity when using the laboratory drier. In an attempt to keep the dilution constant, the defrosted egg used in the storage study was dried after addition of an equal volume of water. This effected an excessive reduction in the viscosity of freshly frozen egg and, to obtain a dry powder, less material could be put through the drier with a corresponding increase in outlet temperatures (150° to 155° F.). However, it was possible from previously available data, some of which have been published (9), to correct the values for the analytical measurements on these samples to values that would be expected at 140° F., thus bringing all measurements to a reasonably comparable basis.

The quality of the powder was assessed by measurements of fluorescence and potassium chloride solution solubility values (4, 7).

Results

The results of the preliminary experiment are given in Table I. When thawed, most of the samples were viscous and had to be diluted before they would flow through the pump and the drier nozzle: the proportions of added water are shown in the table. It appeared from the analytical measurements

TABLE I

EFFECT OF TEMPERATURE AND HUMIDITY ON FROZEN EGG STORED 18 MONTHS BEFORE DRYING

(Drying conditions: inlet temp. 250° F.; outlet temp. 140° F.)

Storage conditions		Dilution necessary for drying, egg : water	Quality of resulting powder	
Temp., ° F.	Relative humidity, %		Fluorescence value	Potassium chloride value
0	Room	1 : 1	25.6	57
	35	2 : 1	19.5	62
	87	2 : 1	19.6	62
15	Room	1 : 1	25.2	65
	35	2 : 1	24.6	61
	87	Undiluted	21.7	63
Unfrozen egg		Undiluted	18.0	73

that prolonged frozen storage had an adverse effect on solubility as assessed by potassium chloride values, and on eating quality as assessed by fluorescence measurements. There was some evidence that a storage temperature of 0° F. was preferable to 15° F. Greatest deterioration seemed to occur in the samples exposed to the room air, but this may have been attributable to the large quantity of water added before drying.

Since dilution may have affected powder quality, it seemed desirable to consider this factor before proceeding to the next phase of the investigation. The results of drying defrosted egg mixed with different quantities of water (Table II) indicated that dilution does affect fluorescence values adversely, but some dilution was necessary if solubility was to be retained. Diluting

TABLE II

EFFECT OF DILUTION OF THAWED FROZEN EGG ON THE QUALITY OF POWDER PRODUCED

(Drying conditions: inlet temp. 250° F.; outlet temp. 140° F. Egg defrosted at 40° F.; time, 48 hr.)

Dilution, egg : water	Fluorescence value	Potassium chloride value
Unfrozen egg		
No dilution	18.9	83.2
5 : 1	21.7	80.0
1 : 1	22.3	78.8
Freshly frozen egg		
No dilution	18.0	67.1
20 : 1	19.0	78.4
7 : 1	26.6	75.4
4 : 1	25.3	73.6
1 : 1	28.5	71.7

fresh liquid egg had only a slight effect on the quality of the subsequent powder. The adverse effects can be partially eliminated if the pump rate is kept constant and the outlet temperature is allowed to vary according to the amount of water present (1). After these trials, it was believed that, to obtain comparable results in subsequent experimental work, the defrosted egg should be diluted with the same proportion of water.

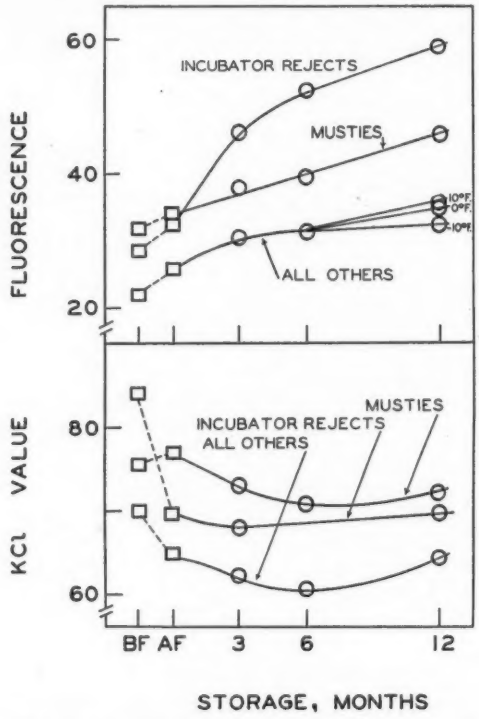

FIG. 1. *The effect of freezing and frozen storage of liquid egg on the quality of powder produced.*

Defrosting: temperature, 40° F.; time 48 hr.

Dilution: one part of defrosted egg to one part water, by volume.

Drying conditions: inlet temp., 250° F.; outlet temperature, 140° F.; except for material dried just after freezing.

B.F.: before freezing: A.F.: after freezing.

The results of the more comprehensive storage experiment are shown in Fig. 1. Since many of the factors studied had no effect on the quality of the powder, measurements to assess these factors were considered as replicates and average values are shown in the figure.

Powders prepared from frozen incubator rejects and musty eggs were definitely of poor quality as assessed by the fluorescence measurement.

However, the solubility of these powders was better than that of powders from Grade *A*, Grade *C*, or cracked eggs. It is possible that enzymic digestion of the protein occurred in the incubator reject and musty eggs and that these processes made the protein fraction more soluble in potassium chloride solution. Failure to differentiate between powders from Grade *A* and Grade *C* or cracked eggs may be attributable to the limited number of samples used or to the changes occurring during freezing. Previous work has shown that Grade

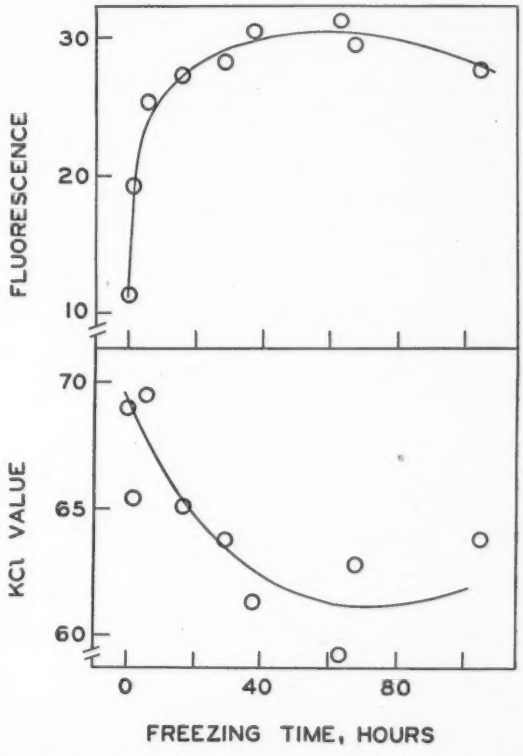

FIG. 2. *The effect of the rate of freezing liquid egg on the quality of the powder produced.*
Defrosting: temperature, 40° F.; time, 48 hr.
Dilution: one part defrosted egg to one part water, by volume.
Drying conditions: inlet temp., 250° F.; outlet temperature, 140° F.

C eggs produce a less desirable powder than Grade *A* eggs (3), and the present experiment indicated that freezing liquid from Grade *A* eggs reduced the quality below that of unfrozen Grade *C* eggs.

The three methods of packaging frozen eggs had no effect on the quality of the powder, and the storage temperatures used affected only the fluorescence values of powder produced from egg stored for 12 months. The values

obtained indicated that storage at $-10°$ F. was preferable, and that there was little difference between temperatures of 0° and $+$ 10° F.

Storage time had a greater effect on the fluorescence values than on the potassium chloride values, although in general, the latter measurements showed a marked loss in solubility as a result of the freezing operation: this decrease in solubility has also been observed in commercial practice. The fluorescence values were slightly greater than those encountered in commercial practice and in the preliminary study. It was believed that these high values may have been attributable to freezing or defrosting techniques. These techniques were subjected to further examination.

Egg is usually frozen commercially in 30- or 40-lb. lots and the operation requires from 24 to 72 hr. depending on the method used. In the preliminary experiment, the small blocks of egg used were frozen within a few hours while in the later experiment a much longer time was required. The results of an experiment to evaluate the effect of freezing rates on the quality of the resultant powder are given in Fig. 2 and show that the quality of the powder becomes progressively poorer as the freezing time is increased from 1 to 20 hr., but that further increase in freezing time had little effect on quality.

In commercial practice, frozen egg is usually pulverized or broken into small fragments that may be mixed with water or fresh egg liquid. The temperature of these liquids is not allowed to exceed 45° F. and defrosting is usually completed in one to four hours. In the preliminary experiment, defrosting

TABLE III

EFFECT OF DEFROSTING TEMPERATURE AND TIME ON THE QUALITY OF POWDER PRODUCED FROM FROZEN LIQUID EGG

(Liquid brought to 40° F.; 15% water added; and dried at inlet temp. of 250° F. and outlet temp. of 140° F.)

Defrosting		Fluorescence value	Potassium chloride value
Temp., ° F.	Time, hr. (approx.)		
100[1]	1	18.9	78.6
80	10	22.0	72.5
70	18	20.6	74.8
60	28	22.6	70.4
50	40	23.8	73.8
40	48	29.0	76.3

[1] *With stirring and container in contact with water; all others without stirring and containers in contact with air.*

was done in water at 100° F. and completed rapidly, but in the later experiment defrosting was done at 40° F. and required about 48 hr. The results in Table III show that rapid defrosting provided a liquid from which an excellent powder could be produced and that long defrosting times gave powders with high fluorescence values. The solubility of the product was affected by other

factors since high solubilities were obtained from both the most rapidly and the least rapidly defrosted egg.

The foregoing results indicate that frozen egg can be used to produce powder of a satisfactory quality. However, the frozen egg should be stored no longer than six months at temperatures of 10° and 0° (if a longer storage time is necessary, storage temperature should be −10° F.); should be frozen and defrosted in a minimum time, preferably about one hour for each operation; and should have the least possible water added when reducing the viscosity for spraying into the drier.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XX. INFLUENCE OF THE INOCULUM ON THE *AEROBACILLUS POLYMYXA* FERMENTATION[1]

By A. C. Blackwood[2] and G. A. Ledingham[3]

Abstract

Whole wheat fermentations were started with known numbers of *Aerobacillus polymyxa* in the range from 50 thousand to 4000 million per ml. of mash. Increasing the initial numbers of the bacteria decreased the lag phase and increased the maximum numbers obtained. Although the initial rate of fermentation was increased, all the fermentations were finished at the same time and gave similar yields of 2,3-butanediol.

The effects of added nutrients, incubation temperature, aeration, and reduced pressure on bacterial growth in the inoculum media were investigated but none of the treatments used had an appreciable effect on the subsequent fermentation. The use of a backstocking technique appears to be a practical method of inoculation.

Introduction

Although certain factors affecting the inoculum in connection with the *Aerobacillus polymyxa* fermentation for the production of *l*-2,3-butanediol have previously been investigated in these laboratories (7, 9), pilot plant operations have shown the necessity for a more detailed study of this problem. It has been found (8) that biotin and a number of amino acids are essential for the growth of this organism and that yeast extract supplies these necessary factors. In a study of various nutrient supplements for starch fermentation by *A. polymyxa*, Fratkin and Adams (4) found that malt sprouts were the most effective. Aeration and reducing the pressure on the fermenting medium were found to increase the fermentation rate and affect the yield of products (1, 2).

The purpose of this investigation is to relate the nutrition and treatment of the inoculum to the actual growth of the culture and to assess the effect of this growth on the production of 2,3-butanediol. The effects of temperature, aeration, reduced pressure, and nutrilites on the inoculum and the effect of the amount of inoculum added and of 'backstocking' on the fermentation have been assessed in comparative experiments.

Materials and Methods

The *Aerobacillus polymyxa* strain used in these experiments was previously isolated in this laboratory and is designated as C3 (2). Stock cultures were carried on wheat agar medium at 30° C.

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The procedures used in preparing inoculum mash (5% finely ground whole wheat or 2.75% commercial starch) and fermentation mash (15% ground whole wheat) have been described previously (9). Three hundred millilitres of fermentation mash in a 500-ml. Erlenmeyer flask was used except in the studies of the effects of amount of inoculum and reduced pressure on the fermentation. In the latter studies it was desirable to remove samples at definite intervals from the fermentation medium without appreciably affecting the surface volume ratio, thus 2.5-litre bottles containing 1 litre of mash were used.

In laboratory practice it has been customary to add a 24-hr. inoculum equal to 3.0% of the volume of the mash. In all experiments designed to test the effects of added nutrient or treated inoculum, both 3.0% and 0.1% additions were studied.

The number of organisms was determined either by the direct count method using a Petroff-Hauser plate or by the standard plating technique. The results given are averages of duplicate tests. Difficulties were encountered with the plate method because of a tendency of the colonies to spread rapidly and though less tedious than the direct count method, dilutions must be made immediately and the results are not available at once. The direct count was used in most cases.

All fermentations were carried out in duplicate. Where 2,3-butanediol analysis was desirable at 48 and 72 hr., four flasks were incubated for each set of conditions and two removed at each time. As fermentation conditions were constant throughout in most experiments only 2,3-butanediol was estimated as an indication of inoculum effect on product yield. In those experiments where the inoculum was aerated or subjected to reduced pressure both 2,3-butanediol and ethanol were determined. The analytical methods employed for the determination of 2,3-butanediol and ethanol have been described elsewhere (9). All analyses were done in duplicate and averages are reported. Microscopic examinations and pH determinations were carried out on each mash to determine the sterility of the fermentation.

Experimental Results

Effect of Amount of Inoculum

The amount of inoculum added ranged from 0.001% to 10% of the mash volume. To obtain the desired concentration of organisms in the inocula, dilutions were made from the original into sterile inoculum medium and 100 ml. was added to 1 litre of the 15% whole wheat mash.

In the first experiment the inoculum contained about 500 million organisms per ml. In the second experiment in order to obtain higher numbers, the inoculum was grown under reduced pressure for 24 hr., then concentrated to half the original volume by centrifuging and discarding the supernatant. This concentrated inoculum contained about 4000 million organisms per ml.

The results (Figs. 1A and 1B) show that the number of organisms added to the fermentation mash greatly influence the growth curve. High initial numbers induced shorter lag periods, shorter logarithmic growth and death periods, and greater numbers of organisms in the medium. These effects

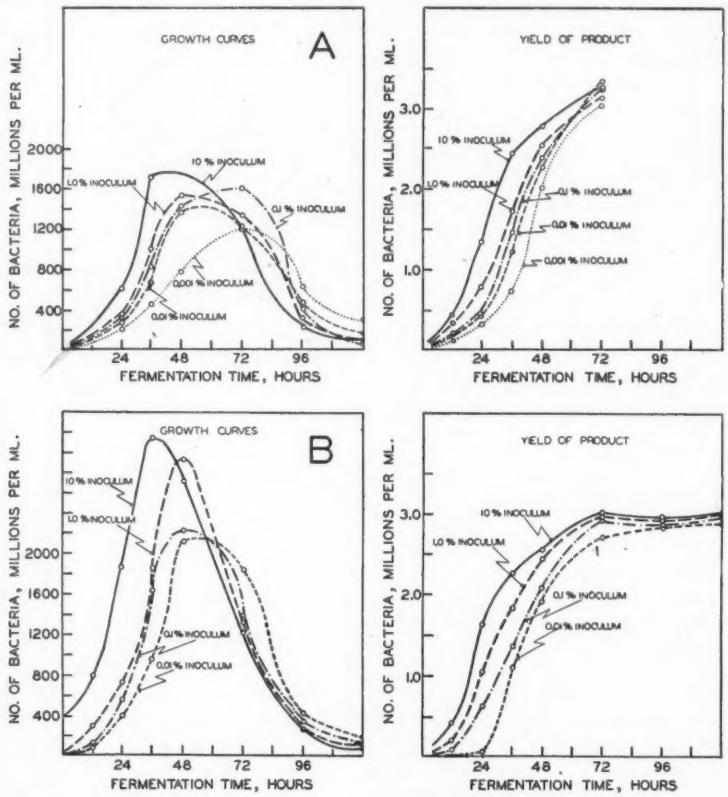

FIG. 1. *The effect of various amounts of inoculum on the growth of the culture and on the 2,3-butanediol yield on a 15% whole wheat mash. A. The inoculum contained 500 million organisms per ml. B. The inoculum contained 4000 million organisms per ml.*

due to inoculum numbers were not quantitatively reproducible as a comparison of the growth curves for the two experiments show. The first three dilutions (10%, 1%, 0.1%) as shown in Fig. 1A contained the same numbers of bacteria as the last three dilutions (1%, 0.1%, 0.01%) shown in Fig. 1B. The relative effect found in each experiment is similar but the actual growth rates and numbers per ml. varied widely. This difference has been found in other experiments and appeared to be uncontrollable. Probably this variable culture activity was the main reason why rate experiments with this organism gave such irregular results.

Marked variations in growth rate did not materially affect the product yield at 72 hr. As the growth rate increased the rate of 2,3-butanediol production also increased. Although the rate of carbohydrate dissimilation was shown to be dependent on the growth rate the amount of 2,3-butanediol produced in all of the samples was similar at 72 hr. However, this was to be expected because if all the carbohydrate is utilized a definite amount of 2,3-butanediol will be produced. A comparison of the growth curves and 2,3-butanediol production in both experiments showed that there was considerable 2,3-butanediol production after the maximum numbers of organisms had been reached. The numbers were still high at 72 hr., but in the second experiment little further 2,3-butanediol was produced, probably because most of the carbohydrate was utilized; however, where 0.01% inoculum was added there was a further increase at 96 hr.

These experiments showed that although the rate of growth and the rate of product formation were closely allied with the amount of inoculum added the yield of product at 72 hr. was not materially affected. Nor was the 2,3-butanediol yield at 72 hr. affected by inherent differences in the ability of the culture to reproduce.

Effect of Nutrient Supplements

The addition of nutrient supplements to inoculum media is known to be advantageous to the growth of this organism when either whole wheat or starch is used as the substrate. The effect of various supplements at specified levels was measured by obtaining population trends in the inocula and by the effect of these inocula on the yield of products in a whole wheat fermentation. As a result of preliminary experiments and a consideration of the value in starch fermentation of various nutrients (4) six nutrient sources were compared: yeast extract (Difco), dried yeast, malt sprouts, Cerogras (dehydrated young oats obtained from the Greenmelk Co., Wallaceburg, Ont.), shorts, and corn steep liquor. Yeast extract was supplied at three levels (0.5%, 1.0%, 1.5%) and all other nutrients were added at the two lower levels.

Table I shows the effect on the population numbers of adding these nutrients to whole wheat inoculation medium. All these nutrients increased the numbers of organisms, with yeast extract showing the greatest effect. On the average, the 1.0% level of nutrient had little more effect than the 0.5% level. Where 1.0% and 1.5% yeast extract was added the growth peak had been passed by 36 hr.

The effect on the population numbers of adding these nutrients to starch inoculation medium is shown in Table II. Here, again, the addition of nutrients increased the number of organisms, with yeast extract giving the greatest effect. However, as starch is deficient in growth supplements the numbers in the control are much lower than found previously with whole wheat medium. The addition of nutrients had only a limited beneficial value.

TABLE I

EFFECT OF ADDED NUTRIENTS AT VARIOUS LEVELS ON THE GROWTH OF *Aerobacillus polymyxa* IN A WHOLE WHEAT INOCULATION MEDIUM

Nutrient	Amount added, %	Number of bacteria (direct count) in millions per ml.		
		12 Hr.	24 Hr.	36 Hr.
Control	0	500	630	1160
Yeast extract	0.5	670	1420	1690
	1.0	850	1780	1300
	1.5	720	1420	1120
Dried yeast	0.5	500	1020	1390
	1.0	580	1180	1240
Malt sprouts	0.5	450	1190	1380
	1.0	500	1290	—
Cerogras	0.5	620	1070	1540
	1.0	660	1330	1750
Shorts	0.5	510	940	1030
	1.0	510	760	—
Corn steep liquor	0.5	570	1010	580
	1.0	430	1010	1280

TABLE II

EFFECT OF ADDED NUTRIENTS AT VARIOUS LEVELS ON THE GROWTH OF *Aerobacillus polymyxa* IN A STARCH INOCULATION MEDIUM

Nutrient	Amount added, %	Number of bacteria (direct count) in millions per ml.		
		12 Hr.	24 Hr.	36 Hr.
Control	0	170	300	250
Yeast extract	0.5	460	600	700
	1.0	490	820	900
	1.5	450	670	1040
Dried yeast	0.5	220	430	710
	1.0	220	460	470
Malt sprouts	0.5	200	210	300
	1.0	200	320	340
Cerogras	0.5	230	310	460
	1.0	240	430	830
Shorts	0.5	380	480	480
	1.0	170	410	400
Corn steep liquor	0.5	300	400	340
	1.0	180	480	470

All of the above inocula with both whole wheat and starch as a substrate were used to inoculate 15% whole wheat mash at two inoculum levels. A statistical analysis of the yields of 2,3-butanediol obtained at 48 and 72 hr. showed that there were no significant variations due to the added nutrients. In Table III the results for the controls and yeast extract only are given. The yield of 2,3-butanediol at 48 hr. decreased in the controls as the inoculum with smaller numbers was added. The addition of yeast extract showed an effect at 48 hr. using starch inoculum but not using the whole wheat inoculum. There were no differences in the yields obtained at 72 hr.

TABLE III

EFFECT OF ADDING YEAST EXTRACT AT THREE LEVELS TO WHOLE WHEAT AND STARCH INOCULUM MEDIA ON THE 2,3-BUTANEDIOL YIELD AT 48 AND 72 HR.

Inoculum medium	Yeast extract added, %	Yield of 2,3-butanediol, %			
		3.0% Inoculum		0.1% Inoculum	
		48 Hr.	72 Hr.	48 Hr.	72 Hr.
Whole wheat	0.0	1.85	2.37	1.72	2.32
	0.5	1.47	2.31	1.91	2.42
	1.0	1.78	2.35	1.46	2.46
	1.5	1.50	2.22	1.88	2.36
Starch	0.0	1.62	2.26	1.42	2.43
	0.5	1.71	2.13	1.57	2.42
	1.0	1.84	2.40	1.61	2.54
	1.5	1.75	2.31	1.70	2.41

Effect of Inoculum Temperature

The optimum fermentation temperature in the range 30° C. to 37.5° C. has been previously reported (9) at 32.5° C. although differences were small and different strains gave varied results. In the present study a wider range of inoculum temperature was chosen (25° C., 30° C., 35° C., 40° C.) to demonstrate more clearly the effect on bacterial growth. Whole wheat inoculum was used both with and without 0.5% yeast extract. Numbers were estimated by the plate count method and are reported in Table IV.

The addition of yeast extract, as previously noted, greatly increased the bacterial numbers except at the highest temperature. After a microscopic examination the lower numbers at the higher temperatures were explained as it was found that as the temperature increased the length of the rods increased. This cessation of cell division while cell elongation continues normally has been reported elsewhere on numerous occasions and was observed to occur spontaneously or as a result of the presence of drugs or other foreign substances (5). This phenomenon was also noted at the end of a very rapid fermentation by *Aerobacillus polymyxa*.

TABLE IV

EFFECT OF TEMPERATURE AND ADDED YEAST EXTRACT ON THE GROWTH OF *Aerobacillus polymyxa* IN A WHOLE WHEAT INOCULATION MEDIUM

Temperature, ° C.	Number of bacteria (plate count) in millions per ml.			
	No nutrient added		0.5% Yeast extract added	
	12 Hr.	24 Hr.	12 Hr.	24 Hr.
25	0.9	4	7.1	44
30	0.2	27	3.5	83
35	0.4	9	0.4	22
40	0.1	17	0.6	8

When the inocula were used to ferment a whole wheat mash there was no significant variation in the 2,3-butanediol yield due to temperature or nutrient at either the 3.0% or 0.1% inoculum level at 48 or 72 hr. The results using 3.0% inoculum are given in Fig. 2.

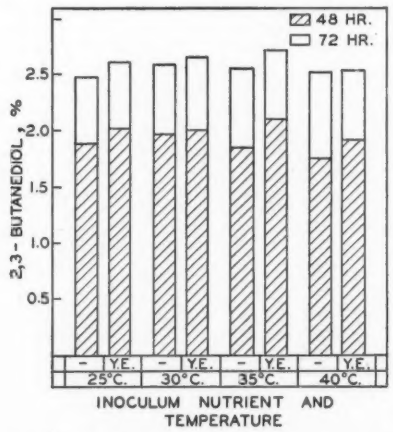

FIG. 2. *The effect of the incubation temperature used on whole wheat inoculum, with and without added nutrient, on the 2,3-butanediol production in a 15% whole wheat mash using 3.0% of inoculum.*

Effect of Aeration and Reduced Pressure

Preliminary experiments indicated that inoculum numbers were increased greatly by aeration or reduced pressure. Table V gives the number of organisms found in whole wheat medium after aeration or reduced pressure for 24 hr. The effect of adding yeast extract was found for each treatment. For the most part, the numbers in the inocula under reduced pressure and aeration were very similar and were approximately double the controls. Yeast extract always increased the numbers. Apparently the higher levels

of aeration and reduced pressure had no further effect but it was suspected that owing to the greatly increased growth rate the period of optimum numbers had been passed at 24 hr.

TABLE V

EFFECT OF AERATION, REDUCED PRESSURE, AND ADDED YEAST EXTRACT ON THE GROWTH OF *Aerobacillus polymyxa* IN A WHOLE WHEAT INOCULATION MEDIUM

Treatment	Number of bacteria (direct count) in millions per ml. at 24 hr.	
	No nutrient added	0.5% Yeast extract added
None	600	1100
Aeration (100 ml./litre/min.)	1150	2600
Aeration (500 ml./litre/min.)	1200	1950
Pressure (20 in. Hg absolute)	1300	1900
Pressure (10 in. Hg absolute)	310	2180

As it was thought that these inocula might have an effect on the ratio of products formed, ethanol and 2,3-butanediol were determined at 72 hr. The results are given in Table VI for the two inoculum levels. At 48 hr. the 0.1% level of inoculum gave lower yields than did the 3.0% level. Aeration of the inoculum gave an increased yield at 48 hr. of 2,3-butanediol at the 3.0% inoculum level but showed little benefit at the lower level of inoculum. When the inoculum numbers under reduced pressure are considered, the yields of 2,3-butanediol were inconsistent at 48 hr., again suggesting that the culture was not in the logarithmic growth phase when used. After 72 hr. fermentation the yields of 2,3-butanediol were practically constant using 3.0% inoculum but were less constant using the 0.1% level and, here, the addition of yeast extract had some effect. The ethanol yields varied little. The effect of aeration or reduced pressure on the inoculum was marked but there was no change in the yield of products in the subsequent fermentation.

A fermentation was carried out under reduced pressure to investigate further the effect on bacterial numbers. Thirty millilitres of inoculum was used to inoculate 1 litre of whole wheat mash in 4-litre bottles. A pressure of 15 in. of mercury was maintained in one flask. The growth curves given in Fig. 3 and the yields of 2,3-butanediol for the first 48 hr. given in Table VII are an average of two experiments.

Bacterial numbers in the control followed the normal type of growth curve but reduced pressure had a great effect on all phases of the curve. The lag period was shorter, the growth rate was more rapid, the period of maximum numbers was short and the death rate was high. Reduced pressure also increased the fermentation rate as the 2,3-butanediol yields show. However,

TABLE VI

EFFECT OF INOCULUM TREATMENT (AERATION, REDUCED PRESSURE, ADDED NUTRIENT) ON THE PRODUCT YIELD IN 15% WHOLE WHEAT MASH

Treatment	Yeast extract, %	48 Hr.	72 Hr.		
		2,3-Butanediol, %	2,3-Butanediol, %	Ethanol, %	Ratio, diol/ethanol
A. 3.0% Level of inoculum					
None	None	1.66	2.57	1.58	1.63
	0.5	1.72	2.58	1.49	1.73
Aeration (100 ml./litre/min.)	None	1.88	2.49	1.50	1.66
	0.5	1.92	2.58	1.53	1.68
Aeration (500 ml./litre/min.)	None	2.13	2.52	1.54	1.64
	0.5	2.21	2.53	1.65	1.53
Pressure (20 in. Hg absolute)	None	1.95	2.41	1.51	1.60
	0.5	1.73	2.36	1.50	1.57
Pressure (10 in. Hg absolute)	None	1.69	2.48	1.52	1.63
	0.5	1.70	2.48	1.53	1.63
B. 0.1% Level of inoculum					
None	None	1.48	2.28	1.30	1.75
	0.5	1.56	2.52	1.52	1.66
Aeration (100 ml./litre/min.)	None	1.42	2.43	1.36	1.79
	0.5	1.91	2.51	1.56	1.61
Aeration (500 ml./litre/min.)	None	1.64	2.38	1.40	1.70
	0.5	1.63	2.44	1.40	1.74
Pressure (20 in. Hg absolute)	None	1.54	2.34	1.29	1.81
	0.5	1.55	2.40	1.42	1.69
Pressure (10 in. Hg absolute)	None	1.37	2.30	1.25	1.84
	0.5	1.59	2.61	1.43	1.82

Adams and Leslie (2) have shown that the final yield of 2,3-butanediol under reduced pressure was lower than normal owing to the induced anaerobic conditions and resulted in a higher ethanol yield with a low 2,3-butanediol to ethanol ratio. The effect of reduced pressure was to increase greatly the actual bacterial population and thus to increase the fermentation rate.

Effect of 'Backstocking'

This method of inoculation has long been standard brewing technique and has been found useful in other fermentations. Preliminary experiments showed that growth was at a maximum between 36 and 48 hr. in the fermentation of 15% whole wheat mash under normal conditions; thus samples taken at 36 hr. were used for inoculum. This ensured that the bacterial culture was still in the logarithmic growth phase.

Inoculum was first prepared in a normal manner and the 3.0% level was used to inoculate the first flasks. The experiment was run in duplicate and the results averaged. After 36 hr., inoculum was obtained from these mashes

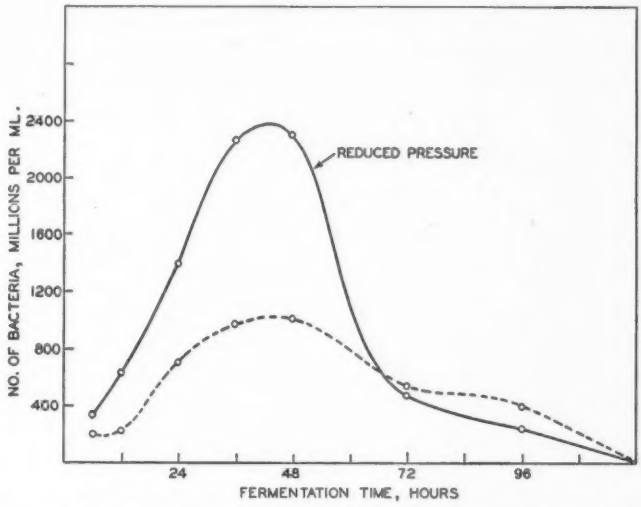

FIG. 3. *The effect of reduced pressure on the bacterial numbers in a 15% whole wheat fermentation mash.*

TABLE VII

EFFECT OF REDUCED PRESSURE ON THE YIELD OF 2,3-BUTANEDIOL (%) IN A 15% WHOLE WHEAT FERMENTATION MASH

	Time in hours				
	6	12	24	36	48
Control	0.41	0.47	0.84	1.13	1.88
Pressure (15 in. Hg absolute)	0.33	0.56	1.22	1.82	2.42

and used to inoculate the second set of flasks. This operation was repeated five successive times. Direct counts and 2,3-butanediol yields were estimated at 36 hr. and 2,3-butanediol content and pH at 72 hr. Aseptic technique was used and there was no evidence of contamination. The results are given in Fig. 4.

Although the inoculum was first grown in inoculum medium this had no effect on the bacterial numbers of the first transfer as compared to those succeeding. There was no increase or decrease in the numbers, pH, or 2,3-butanediol yields through the successive 'backstocking' operations.

Discussion

It is evident that any treatment that produces an increase or decrease in inoculum numbers can be equalled by using more or less of the untreated inoculum, if the treatment has produced no change in the fermentative ability of the bacteria. In all of the fermentation results the yield of 2,3-butanediol at 72 hr. remains unchanged and the effect of a treatment that increased inoculum numbers is only to increase the initial fermentation rate with no effect on the ratio of products formed.

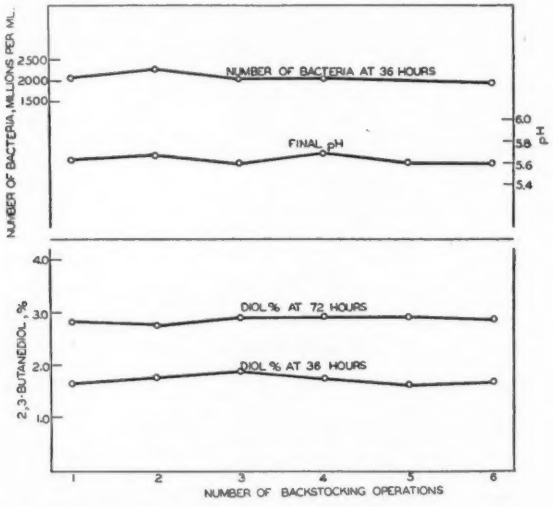

FIG. 4. *The effects of a number of successive 'backstocking' operations on bacterial numbers, final pH, and 2,3-butanediol production.*

In large scale operations the fact that a good yield of 2,3-butanediol is obtained with a small amount of inoculum is very important. Added nutrients are unnecessary, incubation temperature is not critical, and reduced pressure and aeration of the inoculum, while increasing the growth rate, do not affect the product yield; these facts are also of practical importance. Providing aseptic techniques can be applied, 'backstocking' should prove to be a useful and economical operation in this fermentation.

The growth phases of bacteria have been studied for a considerable time and Rahn (10), Buchanan and Fulmer (3), Winslow and Walker (11), Hinshelwood (5), and others have reviewed the literature. The interrelation of the causes of growth and death are not clearly understood. The addition of larger numbers of bacteria to the fermenting medium is known to decrease the 'lag' phase and our results show this (Fig. 1). Rahn (10, p. 402) has shown that the effect of a small inoculum was only to lengthen the time taken to reach the maximum numbers obtained with a large inoculum. This was

found in our results but, in addition, there was a marked increase in the maximum numbers attained as greater initial numbers were added. It is difficult to suggest a logical reason for this phenomenon.

The rate of autolysis is inversely related to the growth rate and is thus faster where the larger amounts of inoculum are used. At maximum numbers the amount of 2,3-butanediol formed is always about 2% but it is not clear whether the rapid death rate is due to accumulation of toxic products, exhaustion of the substrate, or an interaction of these factors. It is improbable that a lack of nutrient and carbohydrate sources can alone explain the effects found although Jordan and Jacobs (6) have shown in their controlled experiments that bacterial numbers varied directly as the food supply.

There is a considerable production of 2,3-butanediol in the 'death' phase. The slower fermentation rate in this phase is found where the larger inoculum is used and thus the benefits of using a large inoculum are nullified. If it were possible to obtain maximum product yields at the same time as maximum numbers are found, the benefit of the larger inoculum would be considerable. A better understanding of the factors affecting bacterial growth might allow this condition to be attained.

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THE FRICTION OF HEATED SLEIGH RUNNERS ON ICE[1]

By P. M. Pfalzner[2]

Abstract

An attempt was made to reduce the sliding friction of sleigh runners on ice at 20° F., 0° F., and −10° F. by applying heat to the runners. The efficiency of this method was found to be less than 20%. Some doubt is thrown on the simple theory that the low friction on ice is due to a lubricating film of water.

Introduction

It is common experience that the friction of ice increases at low temperatures (1; 4, p. 393) and at −140° C. it is of the same order as that found for other unlubricated solids. Sleighs play an important part in transportation in Canada, and it was felt that an attempt should be made to investigate means of lowering the sliding friction on snow and ice surfaces. Two theories have been advanced to account for the ease of sliding on snow and ice at ordinary temperatures, the theory of pressure melting, and the theory of melting due to frictional heating. Klein (2) who has worked with light loadings per sq. in. has favoured the melting-by-friction theory while Wakefield (5) working with higher loadings holds that there is a definite change in the friction after a particular loading is reached under given conditions (3). Again Bowden and Hughes (1) are inclined to support the melting-by-friction theory.

Common to both these theories, however, is the surmise, that some surface melting of the snow or ice occurs, and the resulting thin film of water acts as a lubricant. It would thus appear that, if heat were supplied to sleigh runners, the process of melting at low temperatures would be facilitated, and, it was hoped, that the friction would be substantially reduced thereby. It was decided to make experiments on ice surfaces rather than on snow, since ice is easier to make and is of a more uniform nature than snow.

Description of Apparatus

The experiments were carried out on a turntable driven by an electric motor, the speed being variable by means of a rheostat. On this table a circular track was built into which water was poured and allowed to freeze. The outside radius of the track was 19 in., inside radius 13 in. The surface of the ice was smoothed by a cylindrical heating element that could be lowered to the track; the axis of the cylinder was horizontal and at right angles to the direction of motion of the surface. It was found that the water formed by the melting of the ice had to be dried off, otherwise it was inclined to freeze again and the surface was not properly finished. The drying of the ice could

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[2] *Physicist.*

conveniently be done with a cotton cloth soaking up the water on the turntable just beyond the heated cylinder. Small model sleighs were used, about $3\frac{1}{2}$ in. long, $2\frac{3}{4}$ in. wide, having two nichrome runners, $\frac{1}{8}$ in. wide through which electric current could be passed. The sleigh was attached to a fixed point by a calibrated spring, thus being held stationary on the moving ice track, while the extension of the spring gave a measure of the friction between the ice and sleigh runners.

Experimental Method

A known load was placed on the sleigh, and the turntable set in motion at a rate of about 40 to 60 r.p.m. The extension of the spring holding the sleigh was read, first without passing any current through the runners, then with currents from 2 to 10 amp. passing. The power input was known, and the power usefully expended in lowering the friction was calculated from the reduction in the frictional force due to the heating current and from the speed of revolution.

It was found that rather less than 10% of the power input was useful; it was then decided to pass the current through the front part of the runners only rather than through their whole length; this resulted in some saving of power input but did not raise the efficiency appreciably.

Results and Discussion

The actual figures obtained during the tests are given below in Table I. The following is an outline of the calculations: the radius of the turntable, measured from the centre to halfway between the runners, was 16 in. The saving in work was therefore $2\pi \times 16/12 \times N \times F$ ft. lb./min., where N is the number of revolutions per minute, and F is the difference in force as measured by the spring when the runners are unheated and when they are heated. The expenditure of electrical energy to get this saving was given by the power supplied in watts, and hence, using the relation 1 ft. lb./min. = 0.0226 w., the efficiency is readily obtained. The important thing to note in Table I is that the electrical energy expended simply disappears for the most part, and no matter how much power is put in, the efficiency at 20° F. is only about 10%, and at most 18% at −10° F. Furthermore the advantage in heating merely the front of the runners instead of the whole is relatively small.

The results were rather unsatisfactory in so far as the existing theory was concerned, because, if the crucial factor in low friction is a film of water, experience in other connections shows that direct heating is more economical than frictional heating. It was decided to take the temperature of the runners by a thermocouple placed in contact with the runners. In Table II temperatures are given with the sleigh on and off the ice at 20° F.

These results show that the runners attain the temperature of melting ice immediately when placed in contact with the ice surface. Although the runners were heated by currents as large as 10 amp., and temperatures of

TABLE I

THE EFFICIENCY OF ELECTRICALLY HEATED RUNNERS

Conditions of experiment	Speed of turntable, r.p.m.	Spring tension			Power saved, w.	Heating current		Power supplied, w.	Efficiency, %
		Runners unheated, oz.	Runners heated, oz.	Difference, oz.		Amp.	Volts		
Whole length of runner heated	45	7.50	6.25	1.25	0.67	6.6	1.1	7.2	9
Temp. 10° F., load 11 lb. approx.	49	9.00	8.00	1.00	0.57	6.6	1.1	7.2	8
Front of runner only heated	34	8.00	7.50	0.50	0.20	6.9	0.2	1.4	14
	39	6.25	5.75	0.50	0.24	9.0	0.25	2.25	10
Temp. 10° F., load 11 lb. approx.	36	7.25	6.50	0.75	0.32	9.0	0.2	1.8	18
Front of runner only heated	39	3.0	2.0	1.0	0.46	9.0	1.3	11.7	4
	39	3.0	2.25	0.75	0.35	6.0	0.8	4.8	7
Temp. 20° F., load 11 lb.	41	3.0	2.5	0.5	0.23	3.0	0.4	1.2	2
	41	3.0	3.0	0	0	2.0	0.3	0.6	0
Front of runner only heated	53	4.25	4.25	0	0	2.0	0.3	0.6	0
	53	4.25	4.00	0.25	0.16	4.0	0.6	2.4	7
Temp. 20° F., load 15 lb.	53	4.25	3.30	0.95	0.52	6.0	0.9	5.4	10
	53	4.25	2.75	1.50	0.94	8.0	1.2	9.6	10
	53	4.00	2.65	1.35	0.89	10.0	1.5	15.0	7
Front of runner only heated	45	4.5	3.5	1.0	0.53	10.0	0.6	6.0	9
	60	4.7	3.7	1.0	0.71	10.0	0.6	6.0	12
Temp. −10° F., load 4 lb.	60	4.8	4.0	0.8	0.57	8.0	0.4	3.2	18
	60	4.8	4.3	0.5	0.36	6.0	0.35	2.1	17

TABLE II

THE TEMPERATURE OF THE HEATED RUNNERS (ICE AT 20° F.)

Heating current		Sleigh off the ice		Sleigh on the ice, moving	
Amp.	Volts	Potentiometer milliamp.	Temp., ° F.	Potentiometer milliamp.	Temp., ° F.
6	0.4	1.36	94	0	32
8	0.6	2.56	144	0	32
10	0.7	4.19	209	0	32
0	0	−0.194	22	−0.140	25

over 200° F. were recorded off the ice, the friction fell very little. It is of interest to note, however, in Table I, that the benefit derived by heating the runners is considerably greater at −10° F. than at +20° F. Hence if this heat can be obtained very cheaply, say by special charcoal burners built into steel runners or by heat from the exhaust of the tractor, an improvement of perhaps 20% might be realized in very cold weather.

Acknowledgments

The author wishes to acknowledge with gratitude the interest shown by Dr. C. D. Niven throughout the course of these experiments, and the most valuable assistance rendered by Mr. S. J. Brunette in building the turntable, assembling the equipment, and working out a method for smoothing the ice surface.

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DRILL FOR DETERMINING THICKNESS OF ICE[1]

By T. D. Northwood[2]

Abstract

A device is described for quickly drilling through ice to determine its thickness. It consists of an electric heater mounted at the tip of a rod long enough to penetrate to the desired depth. The unit drills a half inch diameter hole at the rate of about two feet per minute. It operates from a 6 v. storage battery and requires about the same power as an automobile starting motor.

It was recently required to develop a quick method of measuring the thickness of ice formed on lakes or rivers to determine the maximum load it would bear. The method that seemed most practical was to drill a hole through the ice, noting the depth of the drill up to the moment when it plunged through the ice. Some mechanical drills were tried and found to be moderately successful at temperatures near the freezing point. However, these failed at subzero temperatures, where ice becomes glass-like in hardness. More successful was a heater device that melts a half inch diameter hole in the ice. This was very satisfactory, being capable of drilling through about two feet of ice in one minute.

The construction of the final model is illustrated in Fig. 1. It consists essentially of a rod long enough to penetrate the desired range of thickness, with an electrically heated tip. A 6 v. storage battery was chosen as a convenient, portable source of power. This necessitated a heating element with a resistance of about 0.05 ohms, to dissipate the necessary power. The other components of the electrical circuit have a lower order of resistance, although the brass tubing that forms the outer conductor becomes warm enough to ensure that it does not freeze in.

The heating element is a piece of projector carbon (National No. 587) shaped to fit between the outer tubing and a retaining screw, which is tapped into the central brass rod. Since the carbon becomes red hot, even when immersed in ice water, it must be carefully designed to ensure reasonably long life. A large contact area is provided at each end of the element to avoid overheating at these points and consequent deterioration of both brass and carbon. Otherwise a fairly uniform distribution of heat was found desirable to avoid uneven expansion and cracking.

The retaining screw is held firmly against the bottom of the carbon by a spring at the upper end of the central rod. This maintains a good electrical contact in spite of thermal expansion effects and possible crumbling of the contact surfaces of the electrode. The spring tension may be released by pressing a knob on the handle. This facilitates the removal of the

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[2] *Physicist.*

retaining screw and replacement of the carbon if necessary. In limited trials of the final design in the laboratory the carbon appeared capable of lasting indefinitely. However, it is rather fragile and might be broken by rough handling.

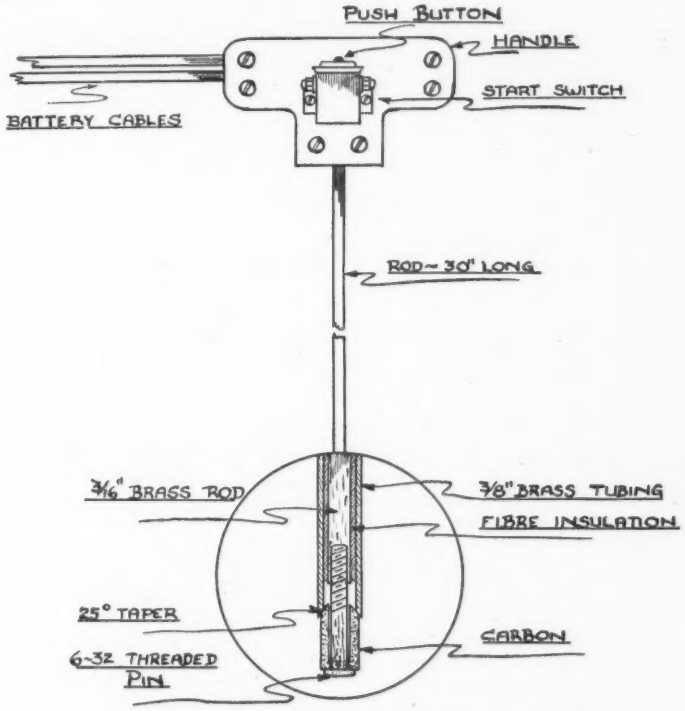

FIG. 1. *Drawing showing essential features of ice-drill.*

Since the electrical load is about equal to that involved in starting an automobile, a standard automobile starting relay was used for switching. This is mounted on the handle in such a way that it may be operated as a push-button. Short flexible cables make connection to a carrying-case containing the storage battery. It is, of course, necessary to re-charge the battery after about a dozen operations.

THE SOLVENT EXTRACTION OF CRUDE MUSTARD GAS[1]

By R. Mungen[2] and H. Sheffer[3]

Abstract

Equilibrium studies with low-boiling hydrocarbon fractions and crude mustard gas indicate that the latter can be extracted to give product purities of approximately 92.5% with 95% recovery. These values have been verified in the operation of a pilot plant for continuous counter-current extraction of crude mustard gas.

One of the simplest and least expensive processes for the manufacture of mustard gas involves the direct reaction of ethylene with sulphur monochloride. A product containing approximately 70% β,β'-dichlorodiethyl sulphide is obtained. Because of the cheapness of the product it is justifiable to purify it by means of an additional process, if material richer in β,β'-dichlorodiethyl sulphide is desired. As part of a general program to attempt to purify the crude material, a solvent extraction process was extensively investigated in these Laboratories.

In 1920 Thompson and Odeen (2) reported an investigation made at Edgewood Arsenal, indicating that some hydrocarbons can be used in the solvent extraction of crude mustard gas to effect a purification. A detailed investigation of equilibrium data and application to pilot plant is described here.

Nature of Crude Mustard Gas

The samples of crude mustard gas used in this investigation were dark brown in colour, contained approximately 70% by weight of β,β'-dichlorodiethyl sulphide, and had melting points ranging from 5.9° to 6.5° C. The impurities present are complex in nature and have not been completely determined. Organic polysulphides as well as free sulphur in a colloidal form are known to be present. Sulphur is readily precipitated on addition of many types of chemicals (e.g. ammonia) to the crude material. During distillation a black tarry residue is formed. In any purification process it would be desirable to avoid decomposition due to excess heating or chemical reaction.

Solubility Studies of Solvents for β,β'-Dichlorodiethyl Sulphide

Studies of the solubility of crude mustard gas in a large number of organic solvents were undertaken to find a suitable solvent for the extraction of β,β'-dichlorodiethyl sulphide. The majority of these liquids were completely miscible with the crude material at ordinary temperatures. Others reacted

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with it, in many cases precipitating sulphur. It was concluded that hydrocarbons in the pentane boiling range were the most suitable solvents for the purification of crude mustard gas.

Extraction Experiments

Single Batch Extractions

Initial extraction experiments were carried out by shaking crude mustard gas with solvent in a separatory funnel. After separation, the solvent layer was removed and analysed.

Crude material, containing 70% by weight of β,β'-dichlorodiethyl sulphide, was extracted with an equal volume of petroleum ether (boiling range 30° to 60° C.). When the solvent was removed from the resulting solvent layer, a product of approximately 80% purity was obtained. From this it is seen that a partial purification can be made using solvent extraction.

Continuous Extraction

A small glass column (1 in. inside diameter, 4 ft. long) was built to study continuous counter-current extraction of β,β'-dichlorodiethyl sulphide from the crude material. The specific gravity of the mustard gas was 1.3 and that of the solvent 0.65. The flow rate of the crude mustard gas feed was 10 ml. per minute and the solvent flow rate was varied to give solvent/feed ratios (by weight) of from 1/1 to 6/1.

It was found that about 85% of the available β,β'-dichlorodiethyl sulphide could be extracted as an 80% pure product using a solvent/feed ratio of 5/1. Using a solvent/feed ratio greater than this increased the yield but reduced the purity of the product.

From this result it was apparent that products of high percentage purity with good recovery could be obtained only from a complete extraction system including rectification. More complete equilibrium data were required to continue work on a pilot plant scale.

Equilibrium Studies

The solvent, chosen from a consideration of cost, availability, and solvent properties was 'Skellysolve *A*,' a mixture of pentanes with a boiling range of 93° to 97° F., 60% boiling at 94° F.

For the equilibrium studies the crude material is considered to be a two component system, β,β'-dichlorodiethyl sulphide (hereafter designated '*H*') and *I* (*I* = impurities). The data are based on the three component system 'Skellysolve *A*'–*H*–*I*.

In order to obtain a wide range of points on the equilibrium curve, it was necessary to have mustard gas samples of a wide range of purities. Samples rich in *H* were obtained by adding extracted material to nearly pure *H* or vice versa. Samples low in *H* and high in *I* content were obtained by continued re-extraction of the crude mustard.

All the batch extractions were carried out at 25° ± 0.01° C. in three-necked flasks, fitted with stirrers. Sufficient quantities of solvent and mustards of various purities were used to give at least 100 gm. of solvent-free extract and residue in each case. After being stirred for 30 min., the contents of the flasks were allowed to settle into two layers. These were carefully sampled after the attainment of equilibrium. The bulk of the solvent in each portion was removed by distillation, the last traces being removed under vacuum. From the weight loss the percentage of solvent was obtained.

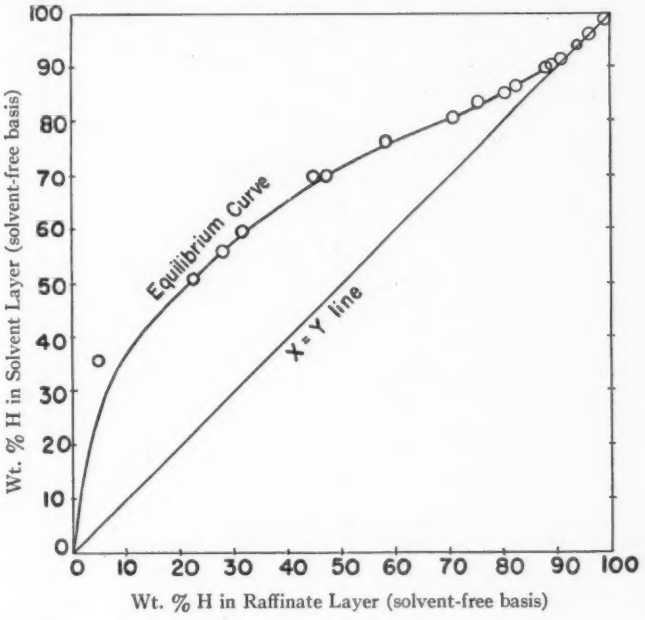
The *H* contents of the solvent-free extracts and raffinates were obtained by means of vacuum distillation using a standardized method. Corrections for impurities carried over during distillation were made on the basis of melting points of the distillates. Verification of the distillation data could be made by means of sulphur analyses, since a straight line relationship was found to exist between total sulphur content and purity of the mustard gas samples. For samples approaching 100% in *H* content, the distillation method gave results with a reproducibility of 0.2%. As the purities were lowered the results were less accurate. Care had to be taken in the distillation of raffinates low in *H* because of decomposition and evolution of gases on heating the material under vacuum. On such samples, therefore, the distillation results may be in considerable error. However, in the case of the raffinate with the lowest *H* content (5%), an error of as much as 100% would not affect the position of the equilibrium curve a great deal.

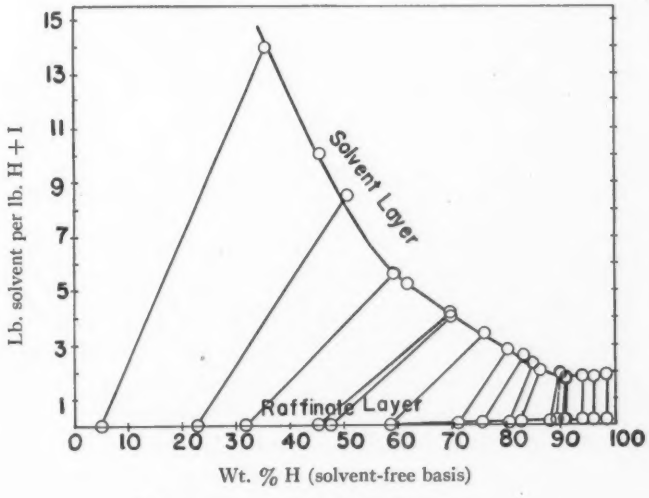
TABLE I

EQUILIBRIUM DATA—SYSTEM 'SKELLYSOLVE *A*'–*H*–*I* AT 25°C.

Composition of extract (solvent layer)				Composition of raffinate (extracted crude layer)			
% *H*	% *I*	% Solvent	% Purity (solvent-free)	% *H*	% *I*	% Solvent	% Purity (solvent-free)
34.0	0.3	65.7	99.1	81.2	0.7	18.1	99.1
33.7	1.3	65.0	96.2	78.8	3.0	18.2	96.3
32.9	2.1	65.0	94.0	76.5	4.9	18.6	94.0
32.8	3.2	64.0	91.2	74.2	7.3	18.5	91.0
31.9	3.1	65.0	91.1	73.6	7.5	18.9	90.7
30.4	3.3	66.3	90.1	74.0	8.9	17.1	89.3
30.0	3.3	66.7	89.9	72.4	9.6	18.0	88.3
27.9	4.4	67.7	86.3	69.3	14.5	16.2	82.7
25.4	4.5	70.1	85.0	68.9	16.6	14.5	80.6
23.0	4.6	72.4	83.3	66.3	21.4	12.3	75.6
21.0	5.1	73.9	80.4	63.1	25.6	11.3	71.1
17.2	5.4	77.4	76.2	53.5	37.9	8.6	58.6
13.9	6.0	80.1	69.9	44.6	49.3	6.1	47.6
13.4	5.8	80.8	69.8	42.1	51.3	6.6	45.1
9.9	6.1	84.0	61.9	—	—	—	—
8.9	6.1	85.0	59.4	30.3	64.7	5.0	31.9
7.2	5.7	87.1	55.8	27.1	69.3	3.6	28.1
5.4	5.2	89.4	50.9	22.0	74.3	3.7	22.9
4.1	4.9	91.0	45.7	—	—	2.9	—
2.4	4.3	93.3	35.5	4.9	92.6	2.5	5

The equilibrium data are given in Table I and are represented graphically in Figs. 1 and 1*a*.





FIGS. 1 and 1*a*. *Equilibrium data. System 'Skellysolve A'–H–I at 25° C.*

Pilot Plant Application of Equilibrium Studies

The method of treating the equilibrium data was that given by Maloney and Schubert (1). The equilibrium data were used to calculate the operational variables of the extraction column. These include solvent dosage, reflux ratio, and number of transfer units for a given separation. The results of these calculations based on enlargements of Figs. 1 and 1*a* are given in Table II. Figs. 2, 3, and 4 give the number of theoretical contact units for recoveries of 85, 90, and 95% at purities of 85, 90, and 92.5%.

TABLE II

T.C.U.'S AS A FUNCTION OF REFLUX RATIO FOR VARIOUS H RECOVERIES, B, AND PRODUCT PURITIES, X_E

Reflux ratio		X_E = 92.5%			X_E = 90%			X_E = 85%		
	B	85	90	95	85	90	95	85	90	95
	X_R	29.4%	21.9%	12.5%	31.2%	23.5%	13.5%	35.0%	27.1%	16.1%
4	$m + n$	27.4	27.8	28.5	9.4	9.7	10.4	4.3	4.9	5.3
	m	3.4	3.8	4.5	2.6	3.0	3.4	2.0	2.6	3.0
6	$m + n$	21.8	22.2	22.8	8.3	8.8	9.2	3.9	4.3	4.8
	m	2.8	3.2	3.8	2.3	2.8	3.2	1.9	2.3	2.8
8	$m + n$	19.5	19.9	20.3	7.6	8.2	8.6	3.8	4.2	4.6
	m	2.5	2.9	3.3	2.0	2.6	3.0	1.8	2.2	2.6
10	$m + n$	18.9	19.2	19.6	7.4	8.0	8.2	3.7	3.9	4.2
	m	2.3	2.6	3.0	1.9	2.5	2.7	1.7	1.9	2.2
20	$m + n$	17.6	17.9	18.3	6.9	7.5	7.7	3.5	3.7	3.9
	m	2.1	2.4	2.8	1.7	2.3	2.5	1.6	1.8	2.0
∞	$m + n$	16.9	17.2	17.5	6.0	6.8	7.0	3.3	3.5	3.7
	m	1.7	2.0	2.3	1.7	2.0	2.2	1.6	1.8	2.0

T.C.U. = *theoretical contact unit.*
m = *T.C.U's for stripping section.*
n = *T.C.U's for enriching section.*
X_R = *H content of raffinate.*

From the equilibrium data it is apparent that it is not possible to obtain 100% pure β,β′-dichlorodiethyl sulphide from the crude material using a solvent extraction process with pentane fractions as the solvent. The maximum purity that can be expected with a reasonable number of contact units and practical reflux ratio is about 92.5%. From the small column extractions and the equilibrium data it was possible to estimate the height of a theoretical contact unit. This height was found to vary markedly with flow rates, but for practical flows was from 3 to 5 ft.

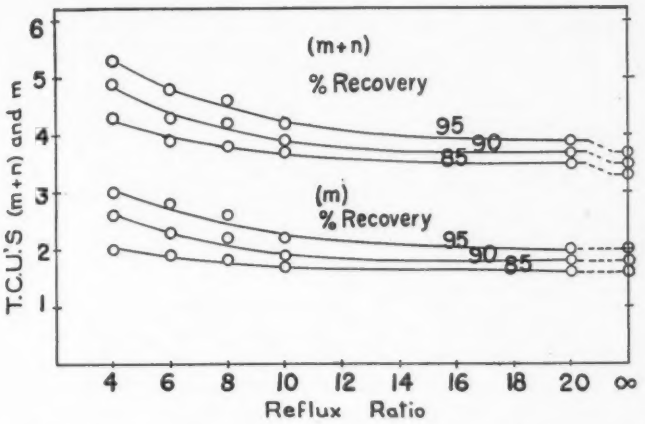


FIG. 2. *Theoretical contact units required to produce 85% product purity as a function of reflux ratio for various H recoveries.*

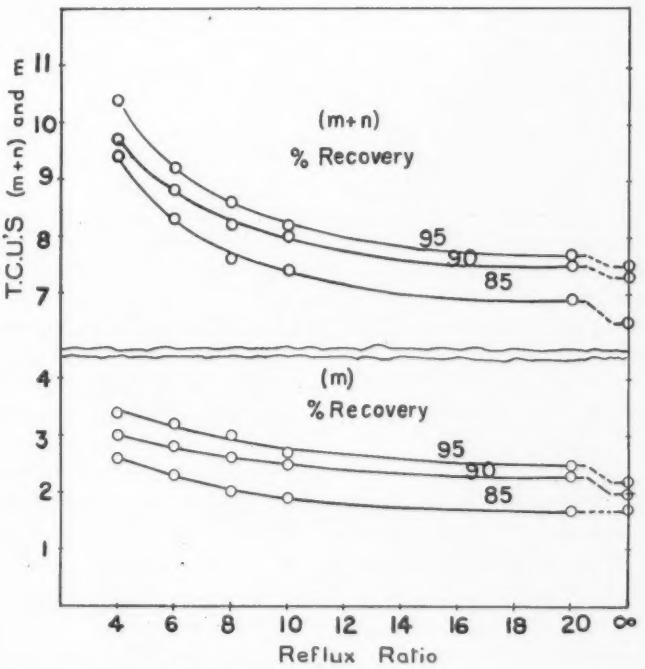


FIG. 3. *Theoretical contact units required to produce 90% product purity as a function of reflux ratio for various H recoveries.*

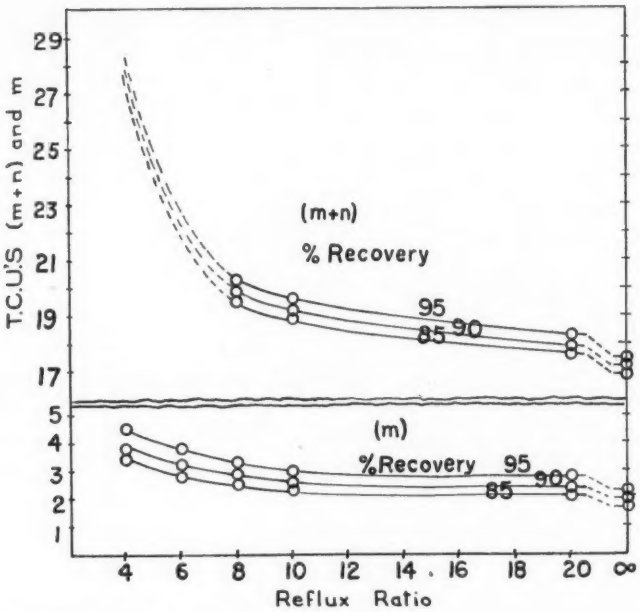


FIG. 4. *Theoretical contact units required to produce 92.5% product purity as a function of reflux ratio for various H recoveries.*

The Pilot Plant

The arrangement of the pilot plant equipment is shown schematically in Fig. 5. The unit was built to accommodate a feed capacity of about 500 lb. per day. The plant was installed in an old ventilation shaft that was of such a height as to allow the installation of about 38 ft. of useful column length.

The extraction column was of standard 4-in. iron pipe assembled from 6-ft. lengths with standard couplings. The packing was $\frac{1}{2}$-in. glass raschig rings. The column was wound with resistance wire over its entire length and insulated with 'rock-wool' to permit temperature regulation. The crude feed entered at the 12 ft. level.

The solvent stripper was made of 14 gauge, 18-8 stainless steel 10 ft. long and 2 in. in diameter. It was fitted with a steam jacket operated at 5 to 10 lb. steam pressure.

The product cooler was a water-jacketed 18-8 stainless steel tube $\frac{3}{8}$-in. I.P.S., 6 ft. in length. The solvent condenser was of the ordinary tube variety made of mild steel. The condenser was 5 ft. long, 6 in. in diameter, and had 17 $\frac{1}{4}$-in. I.P.S. tubes. The cooling water flowed through the tubes.

The feed pump was a Hills-McCanna proportionating pump. The solvent reflux pumps were rotary gear pumps made by the Viking Pump Co.

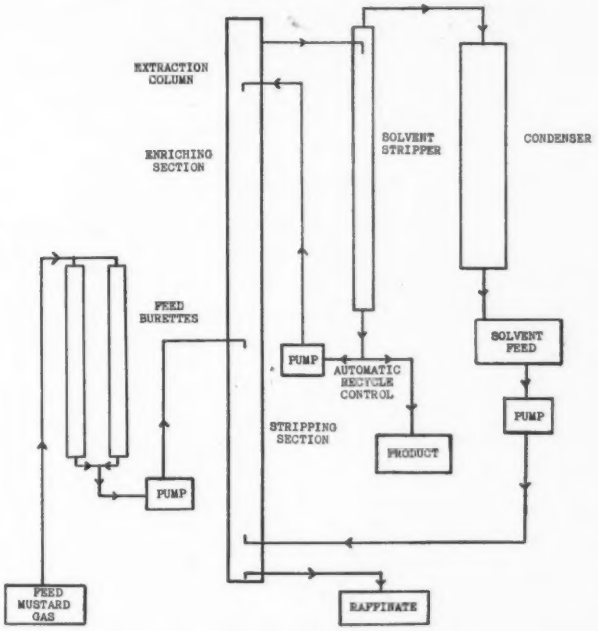


FIG. 5. *Flow diagram, pilot plant.*

The recycle regulator was operated magnetically on a time ratio. Since this is common practice it is not described in detail.

The feed burettes were made of 3-in. I.P.S. mild steel, 4 ft. long, fitted with full length sight-gauges. They were calibrated in 100 ml. units and served to adjust the feed rate of the pump. The two burettes were arranged so that one could be filled while the other supplied the pump with feed liquid. The line from the feed drum to the burettes passed through a glass wool filter to prevent sulphur (often present in the stock) from reaching the pump and interfering with the valve operation.

The product and raffinate receivers were 45-gal. drums fitted with sight-gauges. The solvent receiver and reflux receiver were smaller mild steel drums also fitted with sight-gauges.

The lines and fittings were all of $\frac{1}{4}$-in., $\frac{3}{8}$-in., and $\frac{1}{2}$-in. I.P.S. mild steel. The globe valves were of iron, made by Jenkins Valve Co., Montreal.

The solvent rotameter was a standard Schutte-Koerting model.

Operation of the Pilot Plant

To start operating, crude mustard gas was fed into the column until it appeared in the sight-gauge (12 ft. from bottom of column). The solvent was then pumped in at a slow rate. As the interface began to rise the solvent

rate was increased and the feed rate reduced. The flow rates were gradually adjusted to desired values and the interface kept at a definite level by adjusting the rate of removal of raffinate. Continuous operation was automatic, requiring minor adjustments to flow rates and temperatures. There was no trouble from plugging of lines by sulphur deposits. The raffinate flowed freely.

Results of Continuous Extraction Runs

Table III summarizes the data collected from data sheets for typical runs. The continuous extraction runs demonstrate the effect of varying flow rates, solvent dosage, and reflux ratio. The temperature of the column was kept at 25° C. for all runs. Table III includes calculated H.T.C.U. for the operating conditions used. For Run 17, the feed inlet was moved to the 24 ft. level.

TABLE III

PLANT OPERATIONAL DATA

Run No.		2	6	8	9	10	14	17[1]
Duration of run (hr.)		21	43	29	24	31	68	23
Reflux ratio		4/1	6/1	6/1	6/1	8/1	8/1	3.5/1
Feed rate, ml./min.		100	30	50	70	40	43	50
Feed rate, lb./hr./sq. ft.		205.7	61.7	102.9	143.9	82.3	88.4	102.9
Solvent rate, ml./min.		2000	670	910	1275	910	910	1025
Solvent rate, lb./hr./sq. ft.		1881	630	856	1200	856	856	965
Solvent dosage, lb. solvent/lb. feed		9.2	10.2	8.3	8.35	10.4	9.7	9.4
Crude mustard feed	M.p., ° C.	6.1	6.1	6.1	6.5	6.5	5.9	6.0
	Wt. % *H* content by distillation	70.1	70.1	70.1	70.2	70.2	69.9	70.0
Extract product on solvent-free basis	% Total recovery	73.6	69.8	61.2	58.8	61.0	55.2	80.5
	% *H* recovery	87.2	86.0	77.7	74.4	80.6	72.2	94.2
	M.p., ° C.	9.0	9.9	10.9	10.4	12.0	11.6	8.7
	Wt. % *H* content by distillation	83.1	86.0	89.1	87.5	92.5	91.3	82.2
% Solvent in product		4.3	4.4	4.2	4.4	4.1	4.6	4.3
Raffinate on solvent-free basis	% Total feed	25.8	32.0	39.4	40.2	38.2	46.3	20.0
	Wt. % *H* content	32.9	29.8	38.7	49.3	39.2	45.2	19.5
% Solvent in raffinate		5.2	4.0	5.2	6.3	5.2	5.4	3.1
T.C.U's *m*		1.5	2.2	4.3	3.2	17.0	8.3	1.2
T.C.U's *n*		2.0	2.0	2.0	1.5	2.0	1.8	2.8
H.T.C.U. *m*		16	10.9	5.6	7.5	1.4	2.9	10.0
H.T.C.U. *n*		6	6	6	8	6	6.7	8.6

[1] *Stripping section 24 ft.*
Enriching section 12 ft.
H.T.C.U. = height of theoretical contact unit.

Since the reflux enters at the top of the column a certain fraction of the enriching section is required for mixing. At the bottom the solvent must mix with the raffinate before equilibrium is approached and a portion of the stripping section is used for this purpose. The portion of the column used for mixing is unknown and as a result errors are introduced into calculation of the H.T.C.U.

The time required to reach equilibrium was different for the stripping section as compared to the enriching section. A product of constant melting point would appear in four hours, but the composition of the raffinate would not agree with its calculated value (related to the product) for as long as 24 hr.

The product, containing 4.0 to 4.5% solvent, varied in colour from pale yellow to almost colourless, depending on the purity. The iron and acid contents were negligible. There was a slight deposit of sulphur from extract products of high purity. Occasionally sulphur precipitated from the product in the product cooler, but never in sufficient quantities to cause trouble. This sulphur was most probably carried over by the solvent when high reflux ratios were used and remained in the product when the solvent was removed. Another source of sulphur would be the polysulphides, which may partially decompose on removal of the solvent at 100° C.

Discussion

Pilot plant operation has demonstrated that a maximum purity of approximately 92.5% can be obtained under extreme conditions of reflux, etc., as predicted by the equilibrium data.

An examination of Table III shows that only by accepting low yields and using reflux ratios of 8/1 was it possible to obtain a product approaching maximum purity (Runs 10 and 14). This indicates that the stripping section was of insufficient length to produce good stripping. In Run 17 when the stripping section was 24 ft. long the yield of available β,β'-dichlorodiethyl sulphide was 94%. The column was not long enough to give a product of maximum purity together with good yields.

It is to be noted that the H.T.C.U.-stripping seems to be much less affected by flow rates than the H.T.C.U. in the enriching section. Under favourable conditions (Runs 10 and 14) the H.T.C.U.-enriching is about 3 ft., while the H.T.C.U.-stripping is from 6 to 8 ft. in all the runs.

The complete assessment of the product depends on many factors, including storage trials in weapons. All that can be given here are the β,β'-dichlorodiethyl sulphide contents and melting points as listed in Table III.

Acknowledgment

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